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A TEXT-BOOK OF
QUANTITATIVE CHEMICAL ANALYSIS

FIRST EDITION	1913
SECOND EDITION	1916
THIRD EDITION	1919
FOURTH EDITION	1922
FIFTH EDITION	1928

A TEXT-BOOK
OF
Quantitative Chemical
Analysis

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FIFTH EDITION

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EXTRACT FROM PREFACE TO FIRST EDITION

THIS book is intended primarily for University and College students. We have endeavoured to arrange the book in such a manner that some knowledge of the principles of Quantitative Analysis may be acquired by a practical study of the subjects included in Parts I., II., and III., and that the further requirements of those who are making a special study of Chemistry should be met by the later portions of the book.

Most of the typical exercises in Parts II. and III. may be performed with pure substances, but it is desirable that the student should be accustomed from the commencement of his course to the analysis of substances of "unknown" composition. The serious student finds that this enhances the value of the exercise, whilst the occasional student who "only wants to know the method" has his attention directed to the real purpose of Quantitative Analysis. A list of solutions suitable for analysis is given in the Appendix. In describing typical exercises, care has been taken to give the practical details of manipulation as fully as possible, and where full details are not given, reference is invariably made to the pages where they may be found.

In Part V., all the common elements and radicals are considered, together with the methods for their separation and determination. As the arrangement is alphabetical and copious references to other parts of the book are given, it is hoped that this section will prove a useful index.

In order to avoid constant repetition of particulars in regard to the concentration of reagents, it has been assumed throughout the book that, unless the contrary is stated, the

concentration of a reagent is that specified in the Appendix. The concentrations usually recommended for indicator solutions are such that even "a few drops" is often more than ought to be used. The concentrations recommended in the Appendix are so chosen that 1 c.c. of the indicator is the normal amount required, and throughout the book it is assumed that these dilute indicator solutions are used.

All the diagrams have been specially drawn for the book—in a large number of cases from original photographs of the apparatus.

We desire heartily to acknowledge our indebtedness to Dr Leonard Dobbin, whose helpful counsel has been at our disposal during the preparation of the manuscript.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH,
October, 1913.

PREFACE TO FIFTH EDITION

IN common with the practice followed in every re-issue of this book and to permit of its thorough revision, the entire text has been once more re-set. Many of its pages have been rewritten and, to allow of the inclusion of new matter without materially increasing the size of the book, certain less useful portions have been deleted.

In volumetric analysis the new matter includes the use of titanous chloride as a quantitative reducing agent and of the so-called "adsorption indicators" in the titration of halogen ions with standard silver nitrate solution. The procedure for the calibration of a burette has been modified and the care necessary in the operation emphasised. The burette-reading device described on p. 43 was designed by a student in this laboratory, Mr Maurice Hyman, B.Sc., and we are indebted to him for preparing the diagram (Fig. 25) illustrating this useful accessory in volumetric analysis. Burettes, pipettes, and measuring flasks are now commonly graduated in millilitres—the inscription "ml." replacing that of "c.c."—but the recommendation of a Joint Committee for the Standardisation of Scientific Glassware, in their *Report on Units of Volume*, dated August 1924, that in all scientific publications the term "millilitre" should be used as the unit of volume in place of "cubic centimetre," has not been adopted in chemical literature generally. In this text-book the more familiar if less strictly accurate term "cubic centimetre" has been retained, and the relationship between the cubic centimetre and the millilitre is explained at the appropriate place.

In gravimetric analysis it is pointed out that the determination of potassium as the monohydrate of dipotassium

monosodium cobaltinitrite is applicable in presence of sulphate, and the accuracy of the method now included has been confirmed. Based on many experiments carried out in this laboratory, the procedure for the determination of potassium as perchlorate has been modified and will be found reliable. The description given of the determination of silica in an insoluble silicate has been rewritten, and in the section dealing with the analysis of ores and alloys numerous alterations have been made.

The methods of analysis of organic compounds by destructive hydrogenation, due to Ter Meulen and Heslinga, are briefly indicated.

Our thanks are due to Mr Mowbray Ritchie, B.Sc., for suggested improvements in the manipulation of Hempel's apparatus, and to Dr Oswald J. Walker for directing our attention to Fajans's work on adsorption and its application in volumetric analysis.

We very gratefully acknowledge our indebtedness to Dr Christina C. Miller for providing us with a number of new diagrams, for the careful manner in which she read the whole of the proofs, and for useful suggestions in matters of detail.

September, 1928.

CONTENTS

PART I.—GENERAL PRINCIPLES.

	PAGE		PAGE
Introductory	I	Weighing the Substance	19
The Balance and Weighing	4	Solution of the Substance	22
Calibration of Weights	11	Evaporation	23
Notes on General Apparatus	14	Precipitation	25
Preparation of the Substance for Analysis	16	Filtration	26

PART II.—VOLUMETRIC ANALYSIS.

Introductory	31	STANDARD POTASSIUM PERMAN- GANATE AND DICHROMATE.	
The Measurement of Volumes of Liquids	35	Decinormal Potassium Perman- ganate	77
Standardisation of Instruments	37	Analyses involving the Use of Standard Permanganate—	
General Notes on the Preparation of Standard Solutions	47	Oxalic Acid and Oxalates	81
ACIDIMETRY AND ALKALIMETRY.		Peroxides and Dioxides	81
Introductory	51	Nitrite	83
The Use of Indicators	51	Nitrate	84
Standard Hydrochloric Acid	55	Calcium	85
Standard Sulphuric Acid	60	Manganese	87
Standard Sodium Hydroxide	61	Antimony	89
Standard Barium Hydroxide	64	Decinormal Potassium Dichromate	89
Standard Calcium Hydroxide	65	Analyses involving the Use of Standard Permanganate or Dichromate Solutions—	
Analyses involving the Use of Standard Acid and Alkali—		Iron in Iron Wire	92
Acetic Acid in Vinegar	66	Iron in Ferrous and Ferric Compounds	94
Borax	66	Total Iron in a Mineral	99
Borate in Borax	67	Separate Determination of Fer- rous and Ferric Iron in a Mineral	101
Concentrated Sulphuric Acid	68	Iron in Black Ink	102
Formaldehyde	68	Iron and Chromium in Chrome Iron Ore	102
Solubility of Lime in Water	69	STANDARD SODIUM THIOSULPHATE AND STANDARD IODINE.	
Hydroxide and Carbonate in Lime	69	Decinormal Sodium Thiosulphate	104
Acidic Radical in Salts of Heavy Metals	70	Decinormal Iodine	107
Ammonia (Indirect Method)	70		
Ammonia (Direct Method)	72		
Nitrate	74		
Phosphate	75		

PART II.—VOLUMETRIC ANALYSIS—*continued.*

	PAGE		PAGE
Analyses involving the Use of Standard Iodine and Standard Sodium Thiosulphate—		Decinormal Silver Nitrate and Decinormal Potassium Thio- cyanate	127
Copper	109	Analyses involving the Use of Standard Silver Nitrate and Standard Thiocyanate—	
Sulphurous Acid and Sulphites	111	Chloride, Bromide, and Iodide	129
Sodium Hydrosulphite . . .	111	Chlorate	130
Hydrogen Sulphide	112	Silver	130
Dioxides, Chromates, Chlorates	113	Mercury	130
Available Chlorine in Bleaching Powder	115	Total Chlorine in Bleaching Powder	131
Total Arsenic in Commercial Arsenious Oxide	116		
Antimony	117	VARIOUS VOLUMETRIC PROCESSES.	
Tin in an Alloy	118	Available Chlorine in Bleaching Powder by means of Standard Sodium Arsenite	133
Tin in an Ore	120	Iron by means of Standard Titanous Chloride	134
STANDARD SILVER NITRATE AND POTASSIUM THIOCYANATE.		Zinc by means of Standard Potassium Ferrocyanide .	136
Decinormal Silver Nitrate . .	121	Antimony by means of Standard Potassium Bromate . . .	139
Analyses involving the Use of Standard Silver Nitrate—			
Chloride, Bromide, and Iodide	125		
Cyanide	126		

PART III.—GRAVIMETRIC ANALYSIS.

Introductory	141	Iron as Ferric Oxide	159
Notes on Apparatus	142	Aluminium as Oxide	163
The Gooch Crucible	145	Chloride as Silver Chloride .	164
The Rose Crucible	147	Copper as Cupric Oxide . . .	166
The Ignition and Weighing of Precipitates	148	Zinc as Oxide	168
TYPICAL GRAVIMETRIC EXERCISES.		Sulphate as Barium Sulphate .	169
Water in Magnesium Sulphate Heptahydrate	156	Magnesium as Pyrophosphate .	172
Water in Barium Chloride Crystals	157	Copper as Cuprous Sulphide .	174
Anhydrous Disodium Hydrogen Phosphate in the Crystalline Salt	157	Calcium as Oxalate	176
Iron in Ammonium Iron Alum .	157	ELECTROLYTIC METHODS.	
Other Examples of Analysis by Ignition	158	General	178
		Copper (with Stationary Elec- trodes).	181
		Copper (with a Rotating Cathode)	183
		Nickel	185
		Cadmium	186
		Lead as Dioxide	187

PART IV.—COLORIMETRIC METHODS.

	PAGE		PAGE
Introductory	189	Ammonia	196
Iron	192	Lead	198
Titanium	194	Manganese	199
Copper	195	Nickel	201

PART V.—SYSTEMATIC QUANTITATIVE ANALYSIS.

Aluminium	203	Iron	228
Ammonium	206	Lead	230
Antimony	206	Magnesium	232
Arsenic	207	Manganese	232
Barium	208	Mercury	235
Bismuth	209	Nickel	238
Borate	212	Nitrate	241
Bromide	213	Nitrite	241
Cadmium	213	Phosphate	241
Calcium	214	Potassium and Sodium	244
Carbonate	215	Silica and Silicates	252
Chlorate	221	Silver	257
Chloride	221	Sodium	257
Chromium	221	Sulphate	257
Chromate and Dichromate	222	Sulphide	258
Cobalt	223	Tin	258
Copper	224	Titanium	259
Fluoride	226	Water	260
Hypochlorite	227	Zinc	262
Iodide	227		

PART VI.—THE ANALYSIS OF SIMPLE ORES AND ALLOYS.

Silver Coin	267	Insoluble Silicate	285
Nickel Coin	269	Glass	292
Solder	271	Iron Pyrites	295
Brass	274	Copper Pyrites	297
Bronze	276	Zinc Blende	300
Fusible Alloy	278	Pyrolusite or Manganite	302
Limestone or Dolomite	281	Superphosphate Manure	304

PART VII.—GAS ANALYSIS.

Introductory	308	GAS ANALYSIS WITH HEMPEL APPARATUS.	
Collection of a Sample of Gas for Analysis	309	The Gas-Burette	311
		Absorption Pipettes	313

PART VII.—GAS ANALYSIS—*continued.*

	PAGE		PAGE
Reagents used in Absorption		Zinc Dust	327
Pipettes	315	Available Chlorine in Bleaching	
Manipulation of Apparatus . .	318	Powder	327
Analysis of a Gaseous Mixture .	320		
ANALYSES INVOLVING THE USE OF A		DETERMINATION OF GASES PRESENT	
LUNGE NITROMETER.		ONLY IN TRACES.	
The Lunge Nitrometer	323	General	328
Nitrogen in a Nitrate or Nitrite .	323	Sulphur in Coal Gas	329
Nitrogen in a Nitrite	325	Atmospheric Carbon Dioxide .	331
Hydrogen Peroxide	325	Hydrogen Sulphide in Coal Gas .	334
		Sulphur Dioxide in Flue Gases .	334

PART VIII.—WATER ANALYSIS.

Introductory	335	Nitrite	347
PHYSICAL AND CHEMICAL METHODS		Nitrate	348
OF EXAMINATION AND ANALYSIS.		Phosphate	349
Collection of Samples of Water .	337	Hardness	350
Physical Examination	338	Relative Acidity and Alkalinity	355
Chemical Examination—		Lead	359
Total Solids	340	Action of Water on Lead . .	360
“Free” and “Albumenoid”		Iron	361
Ammonia	341	Saline Constituents	361
Reducing Power	344	Significance of the Results of	
Chloride	346	Analysis of a Potable Water	363

PART IX.—QUANTITATIVE ANALYSIS OF ORGANIC SUBSTANCES.

Combustion Apparatus	366	Modification if Nitrogen is Present	375
Preparation of the Combustion		Modification if Sulphur or a	
Tube	369	Halogen is Present	376
Combustion of a Solid Substance		Nitrogen by Dumas's Method .	377
containing Carbon and		Nitrogen by Kjeldahl's Method .	381
Hydrogen	371	Chlorine, Bromine, and Iodine .	382
Combustion of a Liquid	374	Sulphur	387

PART X.—THE DETERMINATION OF MOLAR WEIGHTS.

Victor Meyer's (Constant Pres-		Beckmann's Boiling-Point Method	406
sure) Method	391	Modification with Electrical	
Lumsden's (Constant Volume)		Heating	409
Method	394	Landsberger's Boiling - Point	
The Freezing-Point Method . .	397	Method	410

APPENDIX.

	PAGE		PAGE
List of Common Reagents . . .	415	Density of Aqueous Alcohol . . .	424
Special Reagents . . .	417	Weight of 1 Litre of Various Dry	
Indicator Solutions . . .	418	Gases	425
Standard Solutions for Analysis .	418	Vapour Pressure of Water . . .	425
Typical Analyses . . .	420	Vapour Pressure of Potassium	
Density and Concentration of		Hydroxide Solutions . . .	425
Various Acids . . .	422	Table of Logarithms . . .	426
Density and Concentration of		Atomic Weights . . .	428
Various Alkalis . . .	424	General References . . .	429
INDEX OF SEPARATIONS			
			433
INDEX			
			435

QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL PRINCIPLES

WHEN the examination of any substance is undertaken for the purpose of determining the respective amounts of any of its constituents, the investigation is known as **quantitative analysis**. The problem may be a simple or a complex one, depending on the nature of the substance, and on whether a complete or only a partial analysis is required. For many purposes it is not necessary to ascertain the amounts of all the constituents of a substance; it may be of importance to determine the amount of only one of them. It is comparatively simple to determine, for example, the amount of iron in an ore, the amount of carbon dioxide in a sample of air, or the amount of chloride in a water supply. On the other hand, it may be necessary to make a complete analysis of a complex ore or rock containing as many as ten or twenty constituents, or to carry out a detailed investigation of a sample of water. The complexity of an analysis depends, however, as much on the nature of the constituents as on their number, and the determination of the amount of even a single constituent may involve a lengthy and refined investigation, demanding the highest skill on the part of the chemist.

Different methods are usually available for the determination of one and the same constituent, but not all of those methods may be applicable to every substance

containing it. The choice of the best method often requires careful consideration.

The gravimetric method of analysis usually involves (1) the separation of the constituents of the substance in the form of insoluble compounds of known composition; (2) the determination of the weight of the compounds so obtained.

The volumetric method of analysis, on the other hand, is based on the use of a reagent of known concentration and on the measurement of the volume of this reagent required to complete the chemical change involved.

A fundamental distinction between the two methods is that *in gravimetric analysis* the constituent that is to be determined must be separated from all the other constituents of the substance; whereas, *in volumetric analysis*, the separation of the constituents is very frequently unnecessary, and one or more of the constituents of a substance can often be rapidly and accurately determined in presence of all the others, thus enormously simplifying the analytical process.

Most substances can be determined either gravimetrically or volumetrically. In the systematic treatment of the subject it is convenient to consider gravimetric and volumetric methods separately; but in practice the two methods of procedure are frequently combined, in order that the analysis may be completed as rapidly and as accurately as possible. When a complete analysis of a complex substance has to be made, the constituents must, as a rule, be separated from one another before the amount of each can be ascertained, and gravimetric methods are usually employed; whereas, if only a partial analysis is required, involving, it may be, only one of the constituents, volumetric methods are often applicable. The latter are almost invariably more expeditious than gravimetric methods, and in analysis for technical purposes where economy of time is often imperative, volumetric methods—not necessarily less accurate than gravimetric—are used as far as possible.

As an example in illustration of some of the foregoing principles, two methods of determining the respective amounts of iron and aluminium in a solution containing ferric and aluminium chlorides may be briefly outlined

(1) In order to accomplish this by gravimetric methods alone, *the iron and aluminium must be separated* by adding an excess of sodium hydroxide to a weighed or measured portion of the solution. The *precipitate*, which consists of ferric hydroxide, is filtered; the *filtrate* contains the aluminium as sodium aluminate.

The *precipitate*, which is contaminated with alkali hydroxide, is dissolved in nitric acid, and ammonia is added in order to reprecipitate the ferric hydroxide. The latter, after filtration, is converted into ferric oxide which is weighed.

The *filtrate*, containing the sodium aluminate, is acidified with hydrochloric acid, and the aluminium is precipitated as aluminium hydroxide by adding ammonia. The precipitate is filtered and, by heating to a high temperature, is converted into alumina which is weighed.

From the weights of ferric oxide and alumina, the respective amounts of iron and aluminium in the solution can then be calculated.

(2) By a combination of gravimetric and volumetric methods, which in this case is much to be preferred, *no separation of the iron and aluminium is necessary*; the procedure is accordingly simpler and more expeditious, and accurate results are more readily obtained.

The iron and aluminium are precipitated together as hydroxides by adding ammonium chloride and ammonia to a weighed or measured portion of the solution, and the precipitate, by heating strongly, is converted into a mixture of ferric oxide and alumina which is weighed. The mixture of ferric oxide and alumina is then dissolved (or another measured portion of the original solution is taken), and the iron in the solution is determined volumetrically. The volumetric process consists, briefly, in reducing the ferric salt to the ferrous state by means of hydrogen sulphide or other suitable reducing agent, and in then determining the amount of iron present by means of a solution of potassium permanganate of known concentration. The aluminium does not interfere with the volumetric determination of the iron.

It is then easy to calculate how much ferric oxide is present in the mixture of ferric oxide and alumina, and the

difference between the total weight of the mixed oxides (which has already been determined gravimetrically) and the weight of the ferric oxide is the weight of the alumina. The respective amounts of iron and aluminium in the original solution can then be calculated.

The Balance.

For accurate analytical work, a suitable balance, capable of supporting a maximum load of 100 to 200 grams in each pan, is indispensable. It is important that the maximum load, whatever it may be, should never be exceeded. With a good balance, properly adjusted and used, very accurate measurements can be made. For example, it is possible to distinguish between two masses of about 10 grams each when they differ in weight by only 0.1 milligram, *i.e.* by 1 part in 100,000. A balance is, therefore, a delicate instrument of precision, and the greatest possible care must be taken in using it. *The rules regarding the use of the balance (p. 9) must be carefully read and thereafter strictly adhered to.*

When weighing in a comparatively rough fashion, it is generally assumed that equipoise is established when the excursions of the pointer towards either side of the mid-point of the scale are of equal amplitude. For the following reasons, however, this method is not invariably adopted in accurate work.

- (1) The zero-point, or resting-point of the unloaded balance, *i.e.* the position which the pointer would apparently take up if the oscillating beam were allowed to come to rest, seldom coincides exactly with the mid-point of the scale.
- (2) Since the oscillating beam, if left to itself, ultimately comes to rest, the amplitude of each oscillation, even when equipoise is established, is *less* than that of the preceding one. It follows that, if an excursion of the pointer to the left is equal to the preceding one to the right, the weight on the right is greater than that on the left (assuming the zero-point to coincide with the mid-point of the scale).

Routine Method of Weighing.

In making a weighing, accurate to 0.1 milligram (0.0001 gram), the following method should be used:—

(1) Find the *zero-point* of the balance.

Release the beam carefully, and if necessary set it oscillating (by wafting air down upon one of the pans) so that the pointer moves through about five scale divisions on either side of the middle point. Close the balance-case *quietly*, and, neglecting the first complete oscillation (two excursions of the pointer), carefully observe and note down the next *three* extreme positions of the pointer, two observations being made on one side and one on the other side of the mid-point of the scale. Assume the scale to be numbered from the extreme left towards the right, *i.e.* from 0 to 20, the mid-point being 10, and estimate tenths of the scale divisions.

If, for example, the observations were

Left.	Right.
(1) 5.0	
	(2) 15.8
(3) 5.4	

the turning-point on the left, corresponding to the point 15.8 on the right, is the mean of 5.0 and 5.4, *i.e.* 5.2, and the resting-point is therefore

$$\frac{5.2 + 15.8}{2} = 10.5.$$

Repeat the observations several times. The results should not differ by more than one or two tenths of a scale division, and the mean is taken as the zero-point of the balance. As the zero-point is frequently subject to slight fluctuations, it should be determined before each set of weighings is commenced.

(2) Place the vessel to be weighed on the *left* pan of the balance and proceed to counterpoise it. It is best to begin with a weight that will probably prove too heavy, as this may save time in the end. For example, if the weight of the vessel is thought to lie between 15 and 20 grams, the latter weight is placed on the right scale-pan. If, on releasing the beam, the 20-gram weight is seen to be too much, it is replaced by a 10-gram weight, and the necessary smaller

weights are added *in regular succession* until finally it is found that, for example, 16.46 grams is too little, whilst 16.47 grams is too much.

In place of the inconveniently small milligram weights, it is preferable, at this stage, to use a rider, which weighs 0.01 gram, whilst its effective weight depends on its position on the divided beam. After some experience it will be found possible approximately to estimate, by observing the extent and rapidity of the oscillation, what additional weight is required to establish equilibrium. If, for instance, it is found that with 16.46 grams on the pan the pointer is deflected slowly to the right whilst with 16.47 grams it is deflected much more rapidly and to a greater extent to the left, the weight of the vessel is nearer 16.46 than 16.47 grams.

Place the rider, then, on the beam, in such a position that equipoise is nearly established—for example, at division 3. Close the balance-case and determine the resting-point. Suppose it is found to be 9.6.

(3) Find the “sensitiveness” of the balance, *i.e.* the displacement of the resting-point produced by an alteration of 1 milligram:—Alter the position of the rider by an amount corresponding to 1 milligram—in such a direction that the resting-point is shifted to the other side of the zero-point—and again determine the resting-point. Suppose it to be 11.1 when the rider is at division 2. The sensitiveness is then equal to

$$11.1 - 9.6 = 1.5 \text{ scale divisions.}$$

(4) Now calculate, as follows, the alteration of the weight necessary to counterpoise the vessel exactly:—

The zero-point—using the figures assumed in the foregoing—is 10.5, and the resting-point with a load of 16.462 grams is 11.1. The vessel weighs, therefore, more than 16.462 grams, the additional amount being equal to that necessary to displace the resting-point from 11.1 to 10.5, or 0.6 of a scale division. Since, however, 1.5 scale divisions correspond to 1 milligram, 0.6 scale division is equivalent to

$$\frac{0.6}{1.5} = 0.4 \text{ milligram.}$$

The weight of the vessel is therefore 16.4624 grams.

The complete weighing thus involves the determination of three resting-points—the first, that observed with the empty balance; the second, after approximately counterpoising; the third, after making an alteration of ± 1 milligram. All the observations made in the above example are shown below:—

Resting-points.

	(1) Unloaded balance.	(2) With load of 16.463 grams.	(3) With load of 16.462 grams.
	5.0	4.4	6.7
	15.8	14.7	15.3
	5.4	4.6	7.0
	<hr/>	<hr/>	<hr/>
Mean	5.2 15.8	4.5 14.7	6.9 15.3
Resting-points	10.5	9.6	11.1
Sensitiveness	= 11.1 - 9.6 = 1.5 scale divisions		
Deviation	= 11.1 - 10.5 = 0.6 „ „		
Additional weight	= $\frac{0.6}{1.5}$ = 0.4 milligram		
Weight of vessel	= 16.462 + 0.4 milligram		
	= 16.4624		

Determination of the Sensitiveness of the Balance with different Loads.

It is evident from the foregoing that the process of weighing may be considerably shortened if the sensitiveness of the balance is already known. The sensitiveness usually varies with the load, and may either increase or decrease with the load, according to the construction of the balance. Good modern balances are so constructed that the sensitiveness is practically constant for all loads up to the limit for which they are intended to be used.

Determine, then, the sensitiveness with 5, 10, 20, and 50 grams in each pan. There is some advantage in placing an excess of 5 mg. on the left scale-pan in order that equipoise may be established with the rider near the middle of the right arm of the balance. The resting-point is then determined with the rider in two positions, differing by 1 or by 2 milligrams, and so chosen that the resting-points are found on opposite sides of the zero-point. From the observations calculate the sensitiveness with each load, that is, the displacement of the resting-point produced by an alteration

of ± 1 milligram, and keep a record of the results in a note-book.

Having determined the sensitiveness in this way, once for all, the process of weighing resolves itself into the following two operations:—

- (1) Find the zero-point of the balance.
- (2) Counterpoise the object to the nearest milligram and find the resting-point.

The fraction of a milligram that must be added (or subtracted) to complete the counterpoise is then calculated. If, for example, the zero-point is 10.2, the resting-point 9.7 with a weight of 5.826, and the sensitiveness 1.7, then the correct weight is $\frac{10.2 - 9.7}{1.7} = \frac{0.5}{1.7} = 0.3$ milligram less than the weight on the balance-pan; that is, 5.8257 grams.

Abbreviated Method of Weighing.

It is often permissible, in practice, to shorten the routine method of weighing and thus to save time, without sacrificing the necessary accuracy. The abbreviated procedure varies with the circumstances, as follows:—

- (1) When the required weight is to be ascertained by “difference,” *e.g.* the difference between (*a*) the weight of an empty vessel, and (*b*) the weight of the vessel and substance, *and when the two weighings involved are consecutive*, the zero-point of the balance may be assumed to be 10 for both weighings. The same error (if any) will appear in both weighings, but the difference will give the accurate weight of the substance.
- (2) When more than 1 gram of substance is to be weighed, the position of the rider may be adjusted by trial until the excursions of the pointer on either side of the mid-point of the scale are of equal amplitude or nearly so. The error involved need not exceed 0.5 milligram, or 0.05 per cent. if the substance weighs 1 gram. This error is usually negligible in comparison with other unavoidable experimental errors (*cf.* p. 21).

Rules to be Observed in Using the Balance.

It should be remembered that one incorrect weighing spoils the whole analysis.

1. The object to be weighed must be at room temperature. If it has been heated, sufficient time must be allowed for cooling. The time required to attain the room temperature varies with the size, etc., of the object, but as a rule twenty minutes is sufficient.
2. Glass vessels, after handling, should be wiped with a soft, dry cloth, and then left in the balance-room for at least twenty minutes before weighing. This is necessary more especially in the case of large vessels, such as flasks, U-tubes, etc., the weight of which may vary by several milligrams according to the conditions under which they are weighed.
3. Never place the substance to be weighed directly on the balance-pan, but place it on a watch-glass or scoop, or in a weighing-bottle. When it is necessary to add more of a solid or liquid, the operation must be performed outside the balance-case.
4. Liquids and volatile solids must be weighed in a closed vessel, such as a stoppered weighing-bottle. If the vapour is corrosive, the vessel should not be opened in the balance-room.
5. Sit opposite the middle point of the balance.
6. Release the beam (and arrest it) gently, and, if necessary, set it swinging by wafting air downwards on one of the pans. The pans must not swing from side to side.
7. Find the zero-point of the balance before each set of weighings.
8. The pointer should move through four or five divisions beyond the mid-point of the scale. The pans must on no account be touched while the beam is swinging.
9. Lift the weights with the forceps only.

10. Before placing anything on the balance-pan, or removing anything therefrom, the balance must be arrested.
11. Always close the balance-case when starting to use the rider.
12. Note the weight in a note-book (not on a loose slip of paper which is apt to be lost) *before* removing the weights from the pan by noting the empty places in the box, and check the weights as they are being removed from the pan. Remove the rider from the beam.
13. Never leave anything on the pans when weighing is finished.
14. Close the balance-case when finished.

Exercises in Weighing.

Read the description given of the routine method of weighing (pages 5 to 8) and, after careful study of the rules to be observed in using the balance, proceed to practise the following exercises, in order to become familiar with the balance and the method of using it. Make notes of your observations and submit them for inspection.

- (1) Find the zero-point of the balance. Repeat the operation four times (at least), arresting the balance after each. Keep a record of your observations as shown on page 7.
- (2) Find the sensitiveness of the balance with loads of (a) 5 grams, (b) 10 grams, (c) 20 grams, (d) 50 grams, in each pan.
Tabulate the results and draw a graph showing the variation of sensitiveness with the load.
- (3) Clean a porcelain crucible and lid. Weigh to 0.1 milligram, (a) the crucible, (b) the lid, (c) the crucible and lid. Keep a record of all the observations from which the zero-point, the various resting-points, and the final results are obtained.

Calibration of Weights.

Since only *weight ratios* and not *absolute weights* are of importance in analytical chemistry, it is not essential that the unit weight adopted should represent a true or standard gram; but it is imperative that the various pieces in a set should agree amongst themselves, *e.g.* that each of the 1-gram weights should be exactly 100 times the weight of each centigram, and one-tenth that of each 10-gram piece. It ought to be an invariable rule to test a set of weights before it is used for accurate work.

The method of "direct weighing" described in the foregoing pages is used in routine analysis, and the accuracy of the results is not impaired although the arms of the balance may not be equal in length—provided the object to be weighed is always placed on the same pan of the balance; but it does not follow that two masses that counterpoise one another are equal in weight; for, evidently, if the lengths of the balance arms are L (left) and R (right), equipoise with two weights W_1 and W_2 on the left and right pans respectively will be established when $W_1L = W_2R$, and $W_1 = W_2$ only if $L = R$.

It is impossible, therefore, to compare the masses of, for instance, two 10-gram weights by a single direct weighing unless the arms of the balance are absolutely equal; and, as this condition is never fulfilled, the method of comparison must be such that the effect of inequality of the arms is eliminated.

The brass weights in a set usually comprise the following pieces:—

50, 20, 10', 10'', 5, 2, 1', 1'', 1'''.

The weights of the same nominal value are usually provided with distinguishing marks; if there are none, one or more *minute* marks must be made upon them with the point of a knife, before beginning the calibration. The comparison of the weights is made by the method of "double weighing" which eliminates the error due to inequality of the arms of the balance. The procedure is as follows:—

Find the zero-point of the balance. Place the 50-gram weight on the left scale-pan and the remainder of the brass

weights on the right. Determine the resting-point. If it differs from the zero-point, find, by the method already described, what additional weight must be added to either side of the balance in order to give exact counterpoise. Now interchange the weights, placing the 50-gram weight on the right, and again determine the difference between the loads. If, for example, the two weighings were

Left.

Right.

$$50 + 2.0 \text{ mg.} = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''',$$
$$\text{and } 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' = 50 + 0.4 \text{ mg.,}$$

the average of the two weighings is

$$50 + 1.2 \text{ mg.} = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''',$$
$$\text{or } 50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' - 1.2 \text{ mg.}$$

In the same way, compare the 20-gram weight with the sum of 10' and 10'', 10' with 10'', and 10' with the sum of 5, 2, 1', 1'', and 1'''.

The effect of inequality of the arms varies with the load, and, if it is found at this stage with 10 grams in each pan that the difference between two weighings is not more than 0.2 milligram, only one weighing need be made in comparing the smaller weights. Proceed then, further, to compare the 5-gram weight with the sum of 2, 1', 1'', and 1'''; the 2-gram weight with 1' + 1'', and also 1'' with 1', and 1''' with 1'.

In the first and second columns of the following table the results obtained with a set of weights are arranged in order, beginning with the small weights.

Nominal value of weights.	Observed results of double weighings.		Calculated value of each piece in terms of weight marked 1'.
		mg.	mg.
1'	=	provisional unit.	= 1'
1''	=	1'	= 1' - 0.1
1'''	=	1'	= 1' + 0.1
2	=	1' + 1''	= 2 × 1' - 0.1
5	=	2 + 1' + 1'' + 1'''	= 5 × 1' - 0.3
10'	=	5 + 2 + 1' + 1'' + 1'''	= 10 × 1' - 0.9
10''	=	10'	= 10 × 1' - 1.1
20	=	10' + 10''	= 20 × 1' - 2.5
50	=	20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 50 × 1' - 6.1
Total 100	=	50 + 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 100 × 1' - 11.0

Now select, as a provisional unit, one of the single gram pieces, say $1'$, and express the value of each of the others in terms of this unit. The result of this is shown in column 3. The transformation is easily made if the successive rows are extended in order, beginning with the first. For instance, the 5-gram weight is equal (see column 2) to the sum of the preceding weights minus 0.2 milligram; but (column 3) the sum of the preceding weights is equal to $5 \times 1' - 0.1$ milligram, therefore the 5-gram weight is equal to $5 \times 1' - 0.3$ milligram.

The choice of a small weight as the unit of comparison throws a big error on the larger weights. In order to secure a uniform distribution of the relative errors, the assumption is now made that the sum of all the weights is exactly 100 grams, and the value of the provisional unit, on this assumption, is calculated.

The sum of the weights,

$$100 \times 1' - 11.0 \text{ milligrams} = 100 \text{ grams,}$$

or $100 \times 1' = 100 \text{ grams} + 11.0 \text{ milligrams,}$

or $1' = 1 \text{ gram} + 0.11 \text{ milligram.}$

The value of the provisional unit, $1'$, is thus 1 gram + 0.11 milligram.

Now substitute this value for each $1'$ in column 3 of the table on p. 12. The following are the results:—

Nominal value	Actual value.		Error.
$1'$	= 1 gram + 0.11 mg.	= 1.0001	+ 0.1 mg.
$1''$	= 1 gram + 0.11 mg. - 0.1 mg.	= 1.0000	<i>nil.</i>
$1'''$	= 1 gram + 0.11 mg. + 0.1 mg.	= 1.0002	+ 0.2 mg.
2	= 2 grams + 0.22 mg. - 0.1 mg.	= 2.0001	+ 0.1 mg.
5	= 5 grams + 0.55 mg. - 0.3 mg.	= 5.0003	+ 0.3 mg.
$10'$	= 10 grams + 1.1 mg. - 0.9 mg.	= 10.0002	+ 0.2 mg.
$10''$	= 10 grams + 1.1 mg. - 1.1 mg.	= 10.0000	<i>nil.</i>
20	= 20 grams + 2.2 mg. - 2.5 mg.	= 19.9997	- 0.3 mg.
50	= 50 grams + 5.5 mg. - 6.1 mg.	= 49.9994	- 0.6 mg.
Total 100		= 100 gms.	± 0.0 mg.

It will be observed that the sum of all the errors is now zero, a necessary consequence of the assumption that the sum of all the weights is equal to 100 grams. The error in the

50-gram piece is now -0.6 milligram, and the minus sign indicates that, when the 50-gram weight is used in a weighing, 0.6 milligram should be *deducted* from the observed weight. It may be noted, however, that in a "difference" weighing, if the same pieces as far as possible are used, the actual error in the result may be nil, or very small, even if the corrections are not applied.

The sum of all the fractions, viz., $.5 + .2 + .1' + .1'' + .05 + .02 + .01' + .01'' + .01'''$ (the rider), is next compared with one of the single gram weights. Finally, the fractions themselves are compared with one another and, if more than negligible differences are found, the errors in the individual fractions are computed in the manner already indicated.

NOTES ON GENERAL APPARATUS.

The following notes are intended to form a guide in the selection of suitable sizes and shapes of certain common pieces of apparatus. The special apparatus required for volumetric and for gravimetric analysis is described in Parts II. and III. respectively.

Wash-bottle.—A 500 to 700 c.c. round flask (Fig. 15, p. 26) is the most convenient size. The jet, which must deliver a fine stream of water, should be within easy reach of the forefinger, in order that only one hand may be necessary to manipulate the wash-bottle (Fig. 16, p. 26). Thick string should be wrapped round the neck of the flask in order to protect the hand when hot water is used.

Beakers.—The most satisfactory beakers for quantitative analysis are made from special resistant glass (*e.g.* Pyrex and Monax glass) and are provided with a spout. The spout is not for convenience in pouring, but it forms an outlet for steam or escaping gas when the beaker is covered with a clock-glass; it prevents the sealing of the beaker with a ring of liquid, portions of which may be projected and lost during boiling. The spout also forms a convenient place at which a stirring-rod may protrude from a covered beaker (Fig. 8, p. 23).

The size of a vessel must be chosen with due regard to the total volume of liquid which it is to contain, *i.e.* neither

too large nor too small: for precipitations in gravimetric analysis, 300 c.c. and 400 c.c. beakers ($4\frac{3}{4}$ to $5\frac{1}{4}$ inches high) are the most generally useful sizes, and for ordinary titrations 200 c.c. and 300 c.c. *conical* beakers (Fig. 1).

Flasks.—Conical flasks (200 to 400 c.c.) with wide mouths (1 inch) are convenient for many purposes.

Casseroles.—Porcelain casseroles (Fig. 2) are used for the same purposes as porcelain basins, and are more convenient to handle.

Funnels.—The most useful sizes are $2\frac{1}{4}$ inches and $2\frac{3}{4}$ inches in diameter. The sides of funnels must be plain, and should enclose an angle of 60° . The stem should be not less than 3 inches long and about 4 mm. in diameter (internal). Funnels with short, wide stems are unsuitable

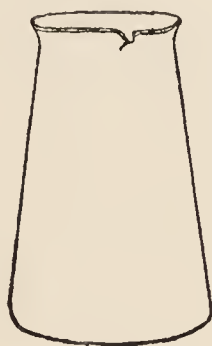


FIG. 1.



FIG. 2.

for general use. Some funnels filter rapidly and others slowly, and the variation in this respect is very marked—often for no very obvious reason. It is worth while testing a number of funnels and selecting the best.

Stirring-rods.—Very light rods for use in beakers may be made from glass *tubing*, 4 to 5 mm. in diameter, by carefully sealing *both* ends in the blowpipe flame. Open glass tubes must not be used as stirring-rods. If made from glass rod, the ends should be rounded in the Bunsen or blowpipe flame. A stirring-rod should be suitable in length for the size and type of the vessel in which it is to be used, *e.g.* 1 inch, at most, longer than the diameter of a basin, or about 2 inches longer than the height of a beaker (Fig. 8, p. 23). If the beaker has no spout and is to be covered with a clock-glass without removing the rod, a shorter rod is required—one that will rest obliquely inside the beaker without touching the clock-glass. Rubber-tipped rods are

used for a special purpose only (see p. 28) and should not be used, as a rule, for stirring solutions.

Boiling-rods.—In order to prevent a boiling liquid from superheating and “bumping,” a boiling-rod may be used. A boiling-rod is made from a piece of glass tubing which is closed at one end, and sealed *near* the other end, as shown in Fig. 3. The open end must be cut off so as to leave a little cup about $\frac{1}{4}$ inch deep, and this end is immersed in the liquid. When the rod is removed, the liquid in the cup-shaped end must be shaken out and the rod rinsed with a jet of water.



FIG. 3.

Desiccators.—A desiccator is used (1) to keep hygroscopic substances dry or (2) to effect the actual drying of wet substances. Dehydration in an ordinary desiccator is a comparatively slow process and requires many hours or even days. An evacuated desiccator is more efficient.

Either concentrated sulphuric acid or lumps of fused calcium chloride may be used as the drying agent. The layer of sulphuric acid should not be more than $\frac{1}{4}$ inch deep, and if the desiccator is in regular use the acid should be renewed occasionally. The ground rim of the desiccator should be greased with vaseline, sparingly used.

Wire Gauze.—Tinned iron wire gauze, 5 inches square with an asbestos centre, is very durable, and forms a satisfactory and flat support for a beaker or flask that is to be heated.

Paper Mats.—By placing beakers and flasks containing liquid, not directly on the bench top, but on paper mats (4 inches in diameter) or on pieces of thick blotting paper, the risk of scratching the glass with sand grains, etc., often the cause of subsequent fracture, is avoided.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS.

Pure Salts.—The salts of commerce described as “A.R.” (analytical reagent) are of a definite standard of purity and may be used without special purification, as a rule, for practising typical methods of analysis and for the preparation of standard solutions.

In the case of a salt of doubtful purity, a good specimen can usually be obtained by recrystallisation. Twenty grams or more of the salt are dissolved in the minimum quantity of hot water contained in a beaker. The hot solution is poured through a fluted filter placed in a funnel with a very short stem ($\frac{1}{2}$ inch), and the clear filtrate is received, with constant stirring, in a porcelain basin which is cooled by placing it in a large dish containing cold water. The fine crystalline "meal" obtained in this way is then separated from the mother liquor by filtration through a Büchner funnel (Fig. 4) in which a circle of hardened filter paper is placed to cover the perforations. The salt is well pressed down in the funnel and the mother liquor removed as far as possible by means of the filter-pump. The crystals are pressed between filter paper and then "air-dried" for twelve hours, first by spreading upon filter paper, and then, as paper is itself hygroscopic, on a clock-glass, dust being excluded. Salts which effloresce must be dried as quickly as possible and bottled.

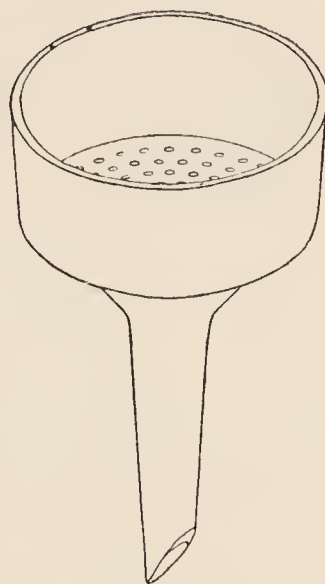


FIG. 4.

Deliquescent salts require special treatment. If the salt contains no water of hydration, it may be dried in a vacuum desiccator; and if it suffers no alteration at 100° or at higher temperatures, it may be dried in the steam-oven or air-oven.

Metals and Alloys.—In the case of the softer metals, pieces suitable for analysis may be cut from the main sample by means of shears, or the metal may be rolled, in a steel rolling-press, into thin ribbon or foil. If this is not practicable, a representative sample should be obtained in the form of borings by means of a steel drill. If the borings are contaminated with oil, they must be washed with ether in a Soxhlet apparatus and then dried.

Minerals, Rocks, and Ores.

Sampling.—In the first place, a sample suitable for analysis must be obtained. If the material is more or less homogeneous, such as a good specimen of a mineral or rock, sampling is comparatively simple, since a small, picked

sample will usually be representative of the whole; whereas, if the material is a bulky, heterogeneous mass, such as a consignment of ore or coal, it is by no means an easy matter to obtain a sample that will represent as far as possible the average composition.

Procedure when an Average Sample is required.—The sampling of ores and other commercial products is a matter of great importance, since their market value is based on the results of the analyses of small samples. Full details of the elaborate methods that are often found necessary in commercial practice cannot be given here, but a general outline of the procedure is as follows:—

- (1) A *large* representative sample is obtained. Any “selection” of pieces different from the average in quality is avoided by taking portions according to some rigid system; for example, a shovelful is taken from each barrow-load or truck-load.
- (2) The large sample is then ground to a coarse powder and thoroughly mixed.
- (3) A smaller sample, say one-quarter or one-sixteenth, of the coarse powder is then more finely ground and the fine powder is thoroughly mixed.

This series of operations—grinding, thorough mixing, and sampling—is continued until a sample of convenient weight for analysis is obtained.

Procedure when a Picked Sample is required.—If the substance is a mineral, a clean sample as free as possible from adhering gangue should be “selected.” By roughly crushing the mineral, it is often possible to detach any material foreign to the mineral proper. In the case of rocks, a few chips broken from a hand specimen will usually be representative. The picked sample, which should weigh about 10 grams, must be powdered.

Crushing and Grinding.—If the material is hard, it is first broken into coarse powder on a hard steel plate (about 4 inches square and $1\frac{1}{2}$ inches thick) with a hardened hammer. Loss of flying fragments is prevented by means of a steel ring (3 inches in diameter and 1 inch high) which is laid on the steel plate.

A "percussion" mortar (Fig. 5) may be used for crushing small lumps. The mortar consists of three pieces—a block (A), a hollow cylinder (B), and a pestle (C)—all of very hard steel. The selected lumps, one piece at a time, are placed in the cylinder (which fits into a depression in the block) and are crushed by striking the pestle with a hammer.

The coarsely powdered substance is then ground in an agate mortar *in very small quantities at a time*.

In order that the decomposition of the mineral by acids or by fusion with alkali carbonates, etc., may be successfully accomplished, a very fine powder is often essential; on the other hand, prolonged powdering is not always necessary and may even lead to error in the analysis. If the mineral contains ferrous compounds, for example, partial oxidation of the iron may occur during the grinding process. Finely ground powders may also take up an appreciable amount of water from the air, and water of hydration may be expelled from minerals by long-continued grinding. Each mineral or rock demands individual treatment in this respect and it is impossible to give general rules.

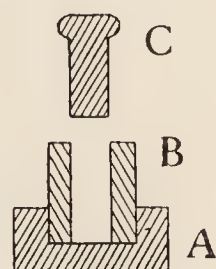


FIG. 5.

WEIGHING THE SUBSTANCE.

The accuracy required in this operation depends on the amount of substance that is to be weighed. If less than 1 gram is to be taken, all weighings ought to be accurate to 0.1 milligram. If several grams are necessary, weigh to the nearest milligram; and if the amount is, say, 10 grams, weigh to the nearest centigram, *i.e.* to 0.005 gram. The weight of the substance is always found by "difference," and is usually determined in one of the following ways:—

- (1) Place 3 to 4 grams of the substance, or a larger quantity if necessary, in a clean, dry weighing-bottle (Fig. 6), and weigh the bottle and its contents. Shake from the bottle (into the vessel in which the next operation is to take place) a quantity that,

judged by the eye, is approximately equal to the amount prescribed, taking care that none of the substance is lost in the process. Weigh the bottle with the remaining substance again. The difference between the two weighings gives the weight of substance taken. It does not matter although the weight is a little more, or a little less, than that desired. If it is considerably less, a further quantity may be shaken out and the second weighing repeated. If it is considerably more, no attempt should be made to return part of the substance to the weighing-bottle, but the whole operation should be commenced

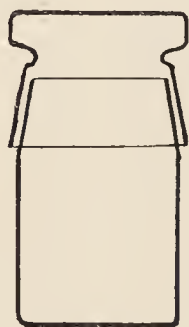


FIG. 6.



FIG. 7.—Scoop for Weighing.

afresh. The bottle should be handled as little as possible between the weighings.

- (2) Weigh a glass scoop. (A watch-glass may be used instead.) With the forceps lift the scoop off the balance-pan, and, with a spatula, place upon it what is judged to be the right quantity of the substance. Re-weigh the vessel and contents. (It saves time in subsequent weighings if the weight of the empty vessel is marked upon it by means of a writing diamond.)
- (3) If the vessel in which the substance is to be dissolved, heated, etc., is comparatively small and light, such as a crucible, weigh the substance directly in the tared vessel.

The first method should be used if several portions of the substance have to be weighed, the separate quantities being successively shaken out of the weighing-bottle which is weighed after each operation.

Liquids and volatile or hygroscopic solids *must* be weighed in a stoppered weighing-bottle.

Vessels that are to be weighed should not be placed directly on the working-bench but on a sheet of clean paper.

**Amount of Substance required for Analysis, and
Limits of Allowable Error.**

Experimental errors are of two kinds: (1) more or less unavoidable errors, depending on the method of analysis employed; and (2) accidental errors, for the most part avoidable, arising from want of care in carrying out the work—including the use of unsuitable or faulty apparatus—or from lack of manipulative skill on the part of the worker. The first class of error can be minimised by the choice of good methods, whilst careful attention to every detail and much practice will help to eliminate errors of the second class.

After the experimental errors have been reduced to a minimum, the percentage error in the final result depends on the amount of substance taken for the analysis. In volumetric analysis, the unavoidable error depends mainly on the precision with which the amount of the standard solution required in the process can be determined. The error in this measurement varies from 0.01 to 0.05 c.c. Taking the higher limit and assuming that only 5 c.c. of the standard solution is required, the error is equivalent to 1 per cent.; but if 25 c.c. is required, the same error in the measurement represents a percentage error of only 0.2. As a general rule, then, the amount of substance taken should be such that from 20 to 30 c.c. of the standard solution is required for each measurement. The total error in volumetric analysis by an accurate method should not exceed 0.3 per cent.

In simple gravimetric analysis, the amount of substance taken should be sufficient to give from 0.2 to 0.5 gram of precipitate in the final weighing. The unavoidable error arising in the course of the work should not, in general, exceed 1 milligram. One milligram represents an error of 1 per cent. if the weight of the whole precipitate is 100 milligrams, but only 0.2 per cent. if the precipitate weighs 500 milligrams. The amount of substance taken, therefore, should not be too small. With

bulky, flocculent precipitates, like ferric hydroxide, which are difficult to filter and wash, the minimum amount of 0.2 gram is desirable; whereas with precipitates like silver chloride or barium sulphate, 0.5 gram, or even 1 gram if need be, is easily dealt with.

In the complete analysis of a complex substance, such as a rock, in which many constituents are present in widely varying proportions, no general rules can be given here; an amount varying from 0.5 to 2 grams is usually suitable.

SOLUTION OF THE SUBSTANCE.

Provided the nature of the substance and solvent allows, the substance is brought into solution in the vessel in which the next operation is to take place. As a rule, either a beaker, a flask, or a porcelain basin is suitable.

In regard to the choice of vessels for quantitative analysis, it should be remarked that the solvent action on glass of water, acids, and more especially alkaline solutions, is considerable, and in exact work it cannot be neglected. The amount dissolved depends on the nature of the glass, and increases with the temperature and with the length of time the glass and liquid are in contact. It is considerably less in the case of glass vessels that have been in use for some time. Porcelain and borosilicate glass resist the action of solvents much better than ordinary glass, and should be used as far as possible in preference to the latter.

If precipitation is to follow solution, the weighed substance is brought into solution in a beaker. Solution may be promoted, if necessary, by heating the beaker (supported on wire gauze) with a Bunsen flame, or by warming on a steam-bath. If actual boiling is required, or if gases are evolved, loss of substance from spirting or spray is prevented by covering the beaker with a clock-glass (Fig. 8). The clock-glass should be, at most, half an inch larger than the mouth of the beaker, and, in order to provide an outlet for steam or escaping gas, the beaker should have a spout. If evaporation is to follow solution, a porcelain basin is used, also covered with a clock-glass of suitable size. In the case of a flask, loss of substance is prevented by placing a small funnel

in the mouth of the flask (Fig. 9), or by clamping the flask in a sloping position. A flask should be used, as a rule, if prolonged heating with volatile acids is necessary, and in

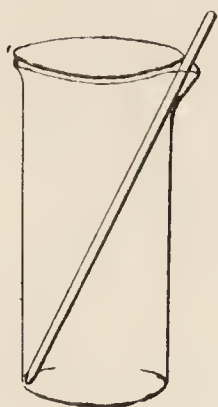


FIG. 8.

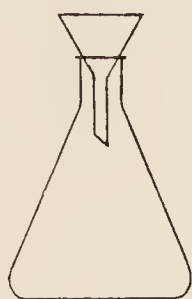


FIG. 9.



FIG. 10.

this case a glass bulb may be placed in the mouth of the flask (Fig. 10).

After solution is complete, or decomposition ended, the cover of the vessel must always be rinsed with a jet of water from the wash-bottle, and the washings added to the solution.

EVAPORATION.

In this operation three points demand special attention, viz. :—

1. No loss of substance must occur in the process.
2. It should take place as rapidly as possible—with due regard to point 1.
3. Contamination from without must be guarded against.

Loss of substance is prevented by evaporating on the steam-bath, thus avoiding actual ebullition of the liquid. As a rule, the process should be conducted in a porcelain basin, not more than two-thirds filled; in a beaker evaporation is slow. Dust, etc., is excluded by placing over the basin a clock-glass, of larger diameter than the basin, supported, *convex side upwards*, on a glass tripod (Fig. 11). The latter is made from thin glass rod, first bending it to form a triangle with sides of 5 to 6 inches, and then attaching legs about $1\frac{1}{2}$ inches long at the corners. (The size depends on the diameter of the basin.)

The rate at which evaporation proceeds depends on the continuous removal of the vapour over the surface of the liquid by means of a current of air, and the operation should therefore be conducted in a good draught. A large excess of steam must be carefully avoided.

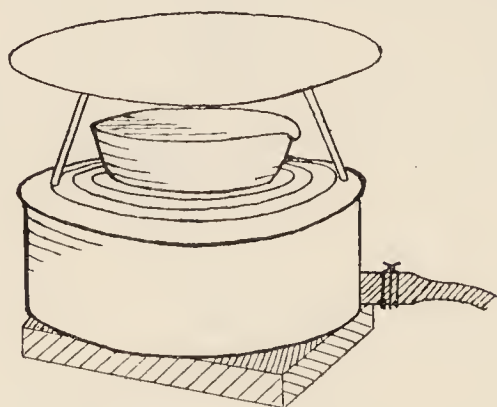


FIG. 11.

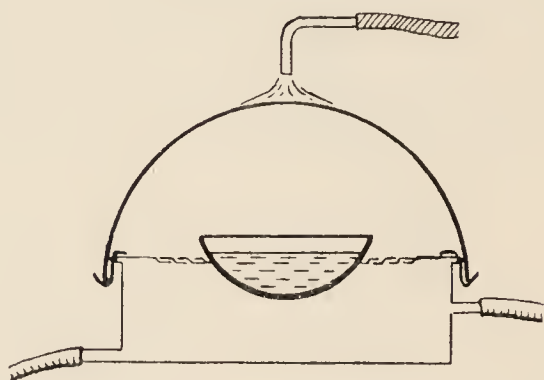


FIG. 12.

It is sometimes necessary to conduct evaporation on a steam-bath in such a manner as to protect the contents of the basin from contamination with impurities, such as sulphur dioxide (from coal-gas flames), ammonia, etc., in the laboratory atmosphere. For this purpose, the arrangement shown in Fig. 12 is both simple and efficient. The hemi-

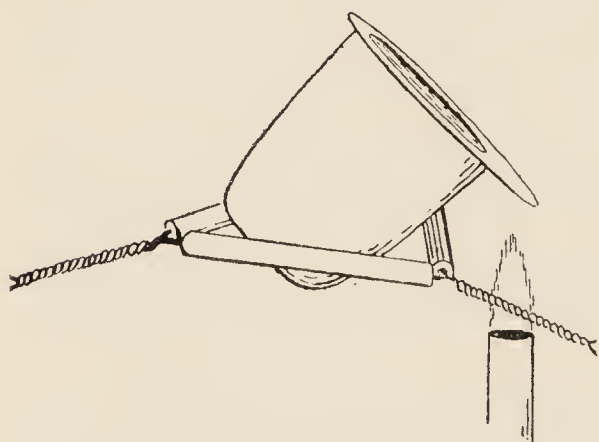


FIG. 13.

spherical condensing cover may be of glass (an inverted glass basin) or, better, of thin copper. One half of a cistern "ball-cock" float, 6 or 8 inches in diameter, makes a satisfactory cover and is easily obtainable. The glass or copper cover is cooled by a stream of tap water. Evaporation by this method is

rapid and, on this account, the arrangement may be used in place of the ordinary plan if a good draught is not available.

Evaporation at the boiling-point may be conducted in a flask, supported obliquely and only half filled. This method is also useful if effervescence due to the escape of gas occurs on heating.

Evaporation of Sulphuric Acid.—The evaporation in a platinum crucible of a liquid of high boiling-point, such as

concentrated sulphuric acid, is conducted with a free flame. In order to avoid loss by spirting and to prevent the liquid from creeping up the side and over the rim, the covered crucible is supported obliquely on a pipe-clay triangle, and the tip of the lid is heated with a small flame (Fig. 13). As the evaporation proceeds, the flame may be brought under the rim of the crucible, but care must be taken that the heating is not too rapid.

Another arrangement is to place the crucible within a capacious iron, nickel, or porcelain crucible fitted with an asbestos ring or an appropriate triangle of iron wire wrapped with platinum foil (Fig. 42, p. 146). The outer crucible, without a cover, is heated over a moderately low flame and forms a hot air-bath which ensures uniform heating of the platinum crucible within.

A useful form of air-bath is shown in Fig. 14. It can easily be made in the laboratory workshop from sheet iron or nickel. The joint is riveted and the base B is secured to A by bending the notched edges over one another. A convenient size is $2\frac{3}{4}$ inches high, $2\frac{3}{4}$ inches wide at the top, and 2 inches at the bottom.

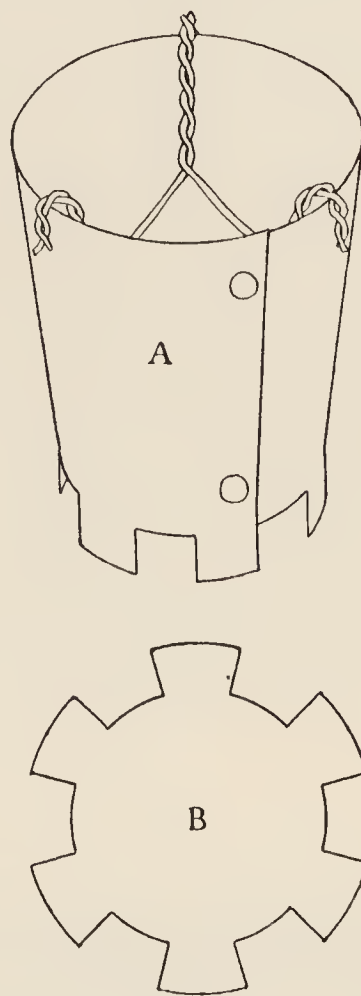


FIG. 14.

PRECIPITATION.

This is generally conducted in beakers. Conical flasks are sometimes preferable, but round flasks are unsuitable. Resistance-glass or porcelain vessels should be used in preference to ordinary glass vessels for precipitations with alkali hydroxides and carbonates and with ammonia. The following general considerations regarding precipitation in quantitative analysis may be noted:—

- (1) The precipitation must be practically complete. In order to secure this, it is usually necessary to adhere more or less rigidly to certain prescribed conditions, such as, for example, the amount of acid present in

the solution. More especially in the case of crystalline precipitates, a certain interval of time must elapse before the precipitation may be regarded as complete, and the filtration must be postponed for one, two, or even for twelve hours.

- (2) The precipitate must be free from contamination with other substances. In spite of all precautions to prevent it, partial precipitation of one substance with another sometimes occurs. In such cases, it is often possible to effect a more or less complete separation by redissolving the precipitate, after filtration, and precipitating a second time.
- (3) The precipitate must be of known composition, or must be capable of easy conversion into a substance of known composition.
- (4) As a rule, a slight excess of the reagent must be added; a large excess is, however, generally prejudicial, and is a common source of error. The reagent should be added carefully, a little at a time, until, after allowing the precipitate to settle, it is seen that another drop produces no further precipitation.
- (5) It is important to note the exact conditions under which certain precipitates are obtained in a granular or coarsely crystalline form, instead of being so finely divided that they are apt to pass through the filter. If, for example, barium sulphate is precipitated in the cold from concentrated solution, it is practically impossible to filter it. A granular precipitate can be obtained in this case, however, by adhering to the following conditions:—(a) the solution must be dilute; (b) it must contain a little hydrochloric acid; (c) it must be heated to the boiling-point; (d) the reagent, barium chloride solution, must also be hot and dilute, and must be added slowly.

FILTRATION.

In quantitative analysis, filtration must be conducted with much greater care than is sometimes given to the operation in qualitative analysis. The more important rules to be observed are the following:—



FIG. 15.—Filtration and Washing by Decantation.



FIG. 16.—Transferring the Precipitate to the Filter.

1. The *size* of the filter depends, not on the volume of the liquid, but on the bulk of the precipitate to be separated. The precipitate must not more than half-fill the filter. As a rule, a filter paper 9 cm. in diameter is large enough, but for bulky precipitates an 11-cm. paper is required.¹
2. The filter paper when folded must be somewhat smaller than the funnel, *e.g.* a 9-cm. paper requires a funnel 5.5 cm. in diameter.
3. It is most important that the folded filter paper should fit the funnel properly. If the funnel angle is not exactly 60° , the paper must be folded with a certain amount of overlap at the second fold so that one cone is larger than the other. In this way a cone of appropriate size can be obtained. The paper is then held in place in the funnel, and, after wetting with water, is well pressed into contact with the funnel wall, especially round the top. This will prevent the entrance of air, and if the stem of the funnel once fills with liquid it will remain full, and the slight suction will effect more rapid filtration.
4. If possible, liquids should be filtered hot.
5. The under side of the rim of the beaker containing the precipitate should be rubbed at one place (opposite the spout) with an almost invisible trace of melted rubber,² and at this place the liquid should be poured down the stirring-rod into the filter, directing the liquid against the side of the filter and not into the apex (Fig. 15). The filter must not be filled quite to the brim.
6. In order to prevent loss by splashing, the stem of the funnel must rest against the side of the receiving vessel.

¹ A special quality of filter paper which has been extracted with hydrochloric and hydrofluoric acids—so-called “ashless” paper—must be used in quantitative analysis. The ash of a single small filter weighs about 0.1 mgrm., and is negligible. Several varieties of “ashless” filter papers are made; for flocculent precipitates, like ferric hydroxide, an open texture paper which filters very quickly is desirable, whereas a paper of closer texture is usually required for fine precipitates like barium sulphate or calcium oxalate.

² Obtained by heating the end of a scrap of rubber tubing in a flame.

Washing of Precipitates.—The separation from a precipitate of the soluble substances present, which filtration roughly effects, is completed by repeatedly “washing” the precipitate—usually with water. In order to accomplish this rapidly and with the minimum quantity of wash-water, the following more or less general rules should be observed:—

Wash with *hot* water, if there is no objection to its use.

Before commencing to filter, allow the precipitate to settle; then, without disturbing the precipitate, pour as much as possible of the clear liquid into the filter.

If the precipitate settles rapidly, wash it several times by “decantation,” as follows:—After the supernatant liquid has been poured through the filter, mix the precipitate with 50 to 80 c.c. of water, allow it to settle again, and once more decant the clear liquid into the filter; repeat the process two or three times. Washing by decantation gives rise to a bulky filtrate and may often be omitted, especially if the precipitate is very small.

Transfer the precipitate to the filter by means of a jet of water from the wash-bottle in the manner shown in Fig. 16. Remove any precipitate adhering to the side of the beaker by means of a stirring-rod tipped with a piece of black rubber tubing, $\frac{3}{4}$ inch long.¹ In place of the glass rod with a rubber tip, a trimmed feather may be used. About 1 cm. is cut off the end of a feather, the plumules are then torn away to within 2 cm. of the end, and those remaining are cut parallel to the quill at a distance of not more than 5 mm. from it.

Be careful not to use so strong a jet of water, or to direct it in such a way that portions of the precipitate are projected out of the filter. Allow each washing to pass through the filter before the next is applied. Wash the margin of the filter paper carefully. Continue the washing until the soluble substance can no longer be detected in the filtrate. Avoid over-washing, as no precipitate is quite insoluble. Towards the end of the process endeavour to collect the precipitate as far as possible in the apex of the filter.

¹ Short rubber tubes, closed at one end, are obtainable for this purpose. Rubber-tipped rods should not be used as stirring-rods and should not be allowed to remain in solutions.

Never put anything but distilled water in the wash-bottle. Separate small wash-bottles (300 c.c.) should be used for ammonia, hydrogen sulphide, alcohol, etc. In order to prevent the backflow of ammonia, etc., to the mouth, a valve may be used. To make the valve, a slit ($\frac{3}{8}$ inch) is cleanly cut in a piece of narrow rubber tubing ($1\frac{1}{4}$ inch). One end of the rubber tube is closed with a plug of glass rod, and the valve is then attached to the blow-tube inside the wash-bottle (Fig. 17).

Use of the Filter-pump.—Accelerated filtration, by means of the filter-pump, is frequently advantageous, especially in the case of bulky, gelatinous, or slimy precipitates like aluminium or chromic hydroxides, or zinc sulphide. The platinum cone which is used to support the filter paper must be well made and in good condition; a bad cone with rough edges is often itself the cause of rupture of the filter paper. In

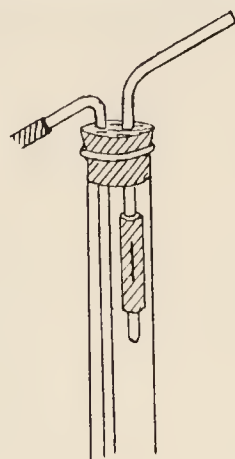


FIG. 17.

place of a platinum cone, one of toughened paper may be used. Gentle suction only should be used,¹ and, unless the filtration is continuous, the suction should be interrupted as soon as all the liquid has passed through. To effect this most simply without stopping the pump, the latter is connected to the filter-flask through a T-piece, one limb of which is closed by a piece of rubber tubing and clip (Fig. 18). When necessary, the clip is opened to admit air. If any cracks or channels form in a bulky precipitate (the result of continuing suction after all the liquid has passed through), close them carefully with a jet of water or with a glass rod.

Instead of the filter-pump, it is often more convenient to use a funnel provided with a looped suction-tube about 20 cm. (8 inches) long and 4 to 5 mm. internal diameter. The funnel stem is cut short, and the suction-tube fused on, as shown in Fig. 19.

In using either the filter-pump or a suction-tube, it is most important that the filter paper should fit the funnel

¹ A pressure regulator for use with the filter-pump is described on p. 147.

properly, and that no air can leak through along the folds of the paper at either side. If air-leakage sets in, the edge of the paper should be firmly pressed into contact with the funnel by means of the stirring-rod. Once suction has been established with a suction-tube, the filter should not be allowed to empty until all the liquid has been filtered.

Paper-pulp Filter.—It is sometimes convenient to filter through paper-pulp, instead of using an ordinary filter paper. A paper-pulp filter is prepared as follows:—Tear a 9-cm. filter paper into small pieces and shake the paper with dilute nitric acid in a small

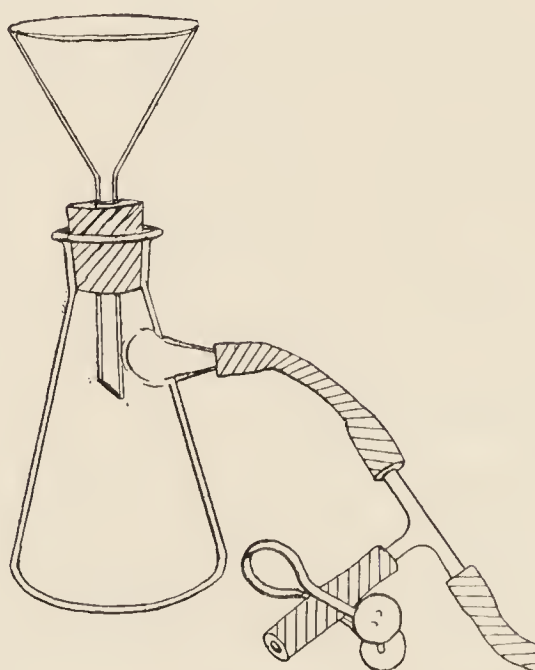


FIG. 18.

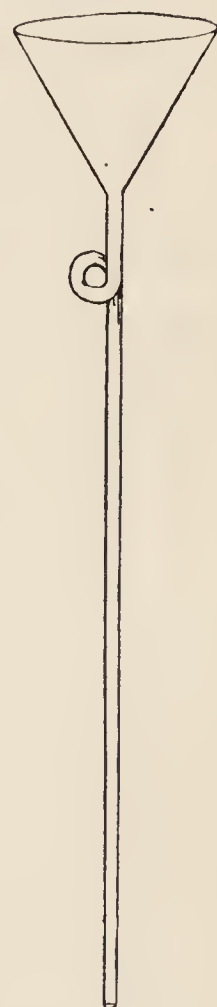


FIG. 19.

flask until it is completely disintegrated. Place a perforated porcelain disc about 2 cm. in diameter in a $2\frac{3}{4}$ -inch funnel, cover the disc with a circle of filter paper, and pour the pulp on the disc, using gentle suction (Fig. 18). Press the pulp down gently with a flat-ended glass rod or with the finger, and wash it with warm water until free from acid. A small Büchner funnel (Fig. 4, p. 17) may be used instead of an ordinary funnel and perforated disc.

PART II

VOLUMETRIC ANALYSIS

VOLUMETRIC methods of analysis, although based on a great variety of chemical reactions, present certain common features, and a quantitative determination by volumetric methods usually involves:—

- (1) The preparation of one or more solutions of accurately known concentration ;
- (2) The use of instruments by means of which the volumes of the solutions employed can be quickly and accurately measured ;
- (3) Some means of recognising the completion of the chemical change involved.

Many volumetric methods are of great practical value on account of their simplicity, rapidity, accuracy, and wide applicability. The following example, omitting certain experimental details, illustrates the general features of a simple determination.

Suppose it is required to determine the amount of sodium chloride in a given solution. A solution of silver nitrate of known concentration is prepared by dissolving an accurately weighed amount of pure silver nitrate in water and making up the solution to a definite volume. A suitable quantity of the sodium chloride solution is accurately measured, a little nitric acid is added, and the silver nitrate solution is run in, in small portions at a time. After each addition of the silver nitrate solution, the mixture is vigorously shaken in order to coagulate the silver chloride and leave the supernatant liquid clear. It is then easy to observe that, when all the chloride has been converted into silver chloride, the addition of another drop of silver nitrate solution produces no further precipitate. This point is called the “end-point” of the interaction. The process involved in the

comparison of one solution with another by a volumetric method such as this is called "titration."

In this way it is possible to determine accurately the *volume* of silver nitrate solution necessary to precipitate all the chloride. Now this volume of silver nitrate solution contains a definite *weight* of silver nitrate which can readily be calculated since the concentration of the silver nitrate solution is known; and since 169.9 grams of silver nitrate interact with 58.46 grams of sodium chloride, it is easy to calculate the amount of sodium chloride in the solution once the weight of silver nitrate equivalent to it is known.

Standard Solutions.—Any solution of accurately known concentration is called a *standard* solution. Standard solutions may sometimes be prepared by dissolving an accurately weighed quantity of the substance in water and making the solution up to a definite volume; *e.g.* standard solutions of silver nitrate and sodium carbonate may be prepared in this way. Often, however, the material to be used contains an unknown amount of impurity, or may be found unsuitable for weighing because it is deliquescent or efflorescent. In such cases, a solution of approximately the required concentration is prepared, and the exact concentration is then found by titration against some suitable substance. For example, a standard solution of sulphuric acid may be prepared by (*a*) making a solution of approximately the desired concentration on the assumption that the concentrated acid contains 96 per cent. by weight of H_2SO_4 , and then (*b*) finding the exact concentration by titration against accurately weighed quantities of pure sodium carbonate.

Normal Solutions.—For the sake of uniformity and especially for convenience in calculations, it is desirable to prepare standard solutions that contain one gram-equivalent (or a simple fraction of the gram-equivalent) of the reacting substance per litre. A solution that contains one gram-equivalent of the reacting substance per litre of solution is called a *normal* solution.

The gram-equivalent of a substance is the weight of the substance, in grams, that is chemically equivalent to 1.008 grams of hydrogen.

A normal solution of hydrochloric acid (which is mono-basic) therefore contains 36.47 grams (the gram-molecular weight, or molar weight) of HCl per litre; a normal solution of sulphuric acid (which is dibasic) contains 49.04 grams (half the molar weight) of H_2SO_4 per litre; and normal solutions of sodium hydroxide and sodium carbonate contain, respectively, 40.01 grams of NaOH and 53.00 grams of Na_2CO_3 per litre.

Many important volumetric methods are based on oxidation and reduction processes, and a normal solution of an oxidising agent is one that is capable of yielding one gram-equivalent, or 8 grams, of "available" oxygen per litre, *i.e.* the weight of oxygen required to oxidise 1.008 grams of hydrogen with formation of water. Potassium permanganate is an example of an oxidising agent which is used in volumetric analysis for the determination of various oxidisable substances. Titrations with potassium permanganate are carried out in presence of an excess of dilute sulphuric acid, and, as the following equation shows, only part of the oxygen of the permanganate is "available" oxygen:



Of the 8 oxygen atoms in 2KMnO_4 , only 5 are "available" for the oxidation of the reducing substance present. Since 2KMnO_4 (316.1 grams) yields 5[O], or 80 grams of available oxygen, a normal solution of potassium permanganate, used as an oxidising agent in the manner indicated, will contain $316.1/10 = 31.61$ grams of the salt per litre.

It may be noted that, as in the case of potassium permanganate, the chemical equivalence of one and the same substance sometimes varies with the type of interaction in which it plays a part. Potassium tetroxalate, for example, may be used for standardising sodium hydroxide solution (see p. 62), and the gram-equivalent is *one-third of the molar weight*, or 84.7, because the molecule, KHC_2O_4 , $\text{H}_2\text{C}_2\text{O}_4$, $2\text{H}_2\text{O}$, contains three replaceable hydrogen atoms; but if the salt is to be used as a reducing agent for standardising potassium permanganate solution (see p. 80), *one-fourth of the molar weight*, or 63.55 grams, is equivalent

to 8 grams of oxygen (or 1 litre of normal permanganate solution) because the oxidation of the molar weight requires 32 grams of oxygen.

Normal solutions are found to be too concentrated for many purposes, and more dilute standard solutions, which may be *seminormal*, *decinormal*, etc., are then used instead. When a standard solution is not exactly normal, the concentration is always expressed in terms of a normal solution. Thus, a solution of hydrochloric acid containing 36.76 grams of HCl per litre is $\frac{36.76}{36.47} = 1.008N$; and a solution of potassium permanganate containing 3.145 grams $KMnO_4$ per litre is $\frac{3.145}{31.61} = 0.0995N$. The symbol "N" is often used as a contraction for normal.

Indicators.—In some titrations, the end-point is indicated by the occurrence of a marked colour change of one of the interacting substances; in others, by the first formation of a permanent precipitate, or by the fact that a precipitate just ceases to form. The addition of a third substance, called an *indicator*, is often necessary in order to make the end-point recognisable.

In titrations with potassium permanganate, no special indicator is required, because the colour of the permanganate is discharged when it is reduced to manganous salt and the progress of the chemical change can readily be followed.

It is possible to titrate a chloride with standard silver nitrate solution without adding an indicator, as described on p. 31, but if the chloride solution is neutral it is more convenient to use potassium chromate as an indicator. When silver nitrate is added to a chromate solution, a bright red precipitate of silver chromate is produced; but if the solution contains both a chloride and a chromate, a permanent precipitate of silver chromate will not form until all the chloride has been precipitated. The production of a permanent red colour thus indicates the end-point.

Volumetric methods involving the determination of acid and alkali are carried out with the aid of indicators, such as litmus, that change colour at or very near the neutral point.

THE MEASUREMENT OF VOLUMES OF LIQUIDS.

For the measurement of the volume of a liquid, various graduated glass instruments are used, the most important being *pipettes*, *burettes*, and *graduated flasks*. *Measuring cylinders* are used for rough measurements only.

Flasks.—Flasks are used in volumetric analysis mainly for the measurement of comparatively large volumes, *i.e.* for volumes of 100 c.c. (cubic centimetres) and upwards. A flask is usually graduated to *contain* a definite volume of liquid.

Pipettes.—A pipette is used to *deliver* one specified volume of liquid. Pipettes are made in various sizes, from 1 c.c. up to 100 c.c. or more. The 10 c.c. and 25 c.c. are the most generally useful sizes.

Burettes.—A burette is used to deliver, not a fixed volume of a liquid, but any specified volume up to its total capacity. For ordinary work a 50 c.c. burette is commonly used, but a 30 c.c. burette, being shorter, is often more convenient.

The Unit of Volume.

The fundamental unit of volume used in measuring the volume of a liquid is the **litre**. The litre is defined, not as a cubic decimetre (the original definition), but as the volume occupied by a quantity of water that will balance the standard kilogram¹ in a vacuum at 4° C. The one-thousandth part of this litre, *i.e.* a **millilitre**, is not exactly equal to the one-thousandth part of a cubic decimetre, *i.e.* a **cubic centimetre**, but for all practical purposes the difference is entirely negligible.²

The measuring instruments employed in volumetric analysis are usually graduated in millilitres (ml.). That unit is still commonly referred to, however, as a cubic centimetre (c.c.), although the instruments themselves are now usually marked ml. instead of c.c. Another unit is sometimes used

¹ The standard kilogram (originally defined as the mass of a cubic decimetre of water at 4° C.) is now, for all purposes, identified with the platinum "Kilogramme des Archives" (kept in Paris) in its actual state.

² The litre, as defined by reference to the standard kilogram, has been found by direct experimental determination to be equal to 1000.027 cubic centimetres, *i.e.* 1 ml. is equal to 1.000027 c.c.

for graduated vessels, viz., Mohr's "cubic centimetre," which is the volume at 17.5°C . of that quantity of water which, when weighed in air with brass weights, has an apparent weight of 1 gram. This unit, which is neither a cubic centimetre nor a millilitre, is better described as the "G.W.A." unit¹ and is 0.2 per cent. larger than the millilitre, *i.e.* 1000 G.W.A. equal 1002 ml. Since in volumetric analysis only relative volumes are required, it is immaterial which unit is adopted, provided it is used for all instruments. To prevent confusion, apparatus graduated in terms of Mohr's unit ought to be marked "G.W.A." and not "ml." or "c.c."

Measuring instruments as bought may be inaccurate. The experimental determination of the errors in the graduation of the instrument is called *calibration*. If the graduations are altered or adjusted so as to make the instrument exact, it is said to be *standardised*. It is now possible to obtain graduated instruments the accuracy of which has been verified at the National Physical Laboratory, Teddington. Measuring instruments of ordinary commercial quality that have not been verified must be standardised or calibrated by the user.

The average temperature of most laboratories is about 15° , and the calibration of the measuring instruments should therefore be made with water at about this temperature.² If it is desired to calibrate a vessel at, for instance, 15° , one requires to know,

- (1) the weight of water that will occupy 1 c.c. at the given temperature (since the density of water varies with the temperature); and
- (2) the corrections to be applied for the weight of air displaced by the water and by the brass weights respectively.

In the table on page 37 the corrections for these factors have been introduced.

¹ The letters "G.W.A." stand for "grams of water in air."

² Since the capacity of glass vessels varies with change of temperature, any graduated vessel can be correct only at one particular temperature. This is termed the standard temperature of the vessel, and 15° is generally used in this country as the standard temperature. A litre flask, the standard temperature of which is 15° , will hold about 1000.1 ml. at 20° .

*Ratio of Weight to Volume of Water, weighed in Air
with Brass Weights.*

Tempera- ture.	Weight of 1 c.c. in grams.	Volume in c.c. occupied by 1 gram.	Tempera- ture.	Weight of 1 c.c. in grams.	Volume in c.c. occupied by 1 gram.
10°	0.9987	1.0013	21°	0.9970	1.0030
11°	86	14	22°	67	33
12°	85	15	23°	65	35
13°	83	17	24°	63	37
14°	82	18	25°	60	40
15°	81	19	26°	57	43
16°	79	21	27°	55	45
17°	77	23	28°	52	48
18°	76	24	29°	49	51
19°	74	26	30°	46	54
20°	72	28	31°	43	57

STANDARDISATION OF A FLASK.

The flask should be provided with a well-fitting ground-in glass stopper, and should have a long, narrow neck. The graduation mark should be on the lower half of the neck (Fig. 20). The diameter of the neck should not exceed 20 mm. for a litre flask, 16 mm. for a 500 c.c. flask, or 12 mm. for a 100 c.c. flask. Flasks are graduated to *contain* definite volumes, but for special purposes a flask may be so graduated that it will *deliver* a measured volume of liquid.

Clean the flask thoroughly¹ and set it aside inverted

¹ **Methods of Cleaning Glass Apparatus.**—If a pipette (or burette) is dirty, drops of liquid adhere to the walls and a considerable error may be introduced. Several methods of cleaning may be used, the choice being largely a matter of personal preference.

1. Wash with sodium hydroxide (to remove grease), then successively with water, dilute nitric acid, and finally several times with water.
2. If the glass is very greasy, alcoholic sodium hydroxide or a mixture of bench sodium hydroxide and alcohol will be found more efficient than the aqueous solution.
3. Soap and water, applied with a cloth or sponge tied to the end of a thin wooden rod, provide about the best method of cleaning a burette.
4. Grease may be removed by prolonged treatment with chromic acid solution (a mixture of potassium dichromate solution and concentrated sulphuric acid). This is slow but efficient. It is best to fill the vessel and set it aside overnight, or as long as possible. A pipette may be kept full by filling almost to the top and closing at once with a cap made from an inch of rubber tubing and a short piece of glass rod.

A pipette or burette is clean if no drops form on the surface of the glass after the liquid is run out.

until it is dry. (This is preferable to drying it in a steam-oven.) Weigh the flask on a suitable balance. (The weighing should be accurate to within 0.01 gram for a 100 c.c. flask and to within 0.1 gram for a litre flask. A special balance, capable of supporting the heavy load, is required for flasks larger than 100 c.c.) Fill the flask to the graduation mark with water at a temperature of from 14° to 16°.

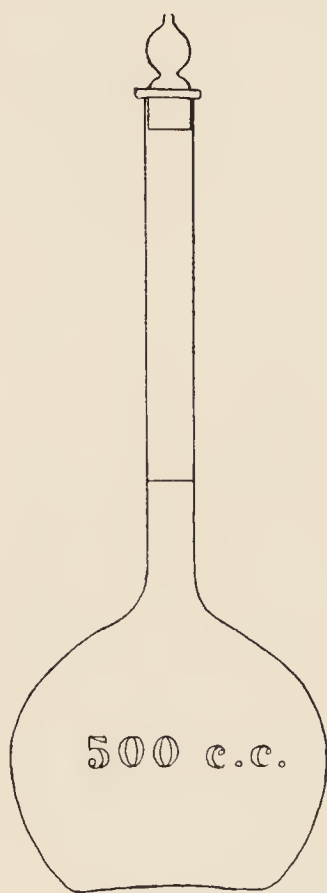


FIG. 20.

Examination of the surface of the water in the neck of the flask will show that it is not flat but curved, and the level of the water must be adjusted so that the lowest point of the curved surface (the meniscus) coincides exactly with the graduation mark. Error due to parallax is avoided when the front and back of the graduation mark are seen as a single line. The meniscus will be clearly visible if a white card is held behind it. The adjustment of the water level is made by adding or removing water with a glass tube drawn out to a capillary. No drops should remain adhering to the glass above the graduation mark, but this will only happen if the glass is greasy.

Weigh the flask filled with water, and, from the weight of the water, calculate the volume.

Example.—The following figures were obtained with a 500 c.c. flask:—

Flask + water	=	566.85	grams
Tare of flask	=	65.20	„
Weight of water	=	501.65	„

The temperature of the water was found to be 14°. From the table on p. 37 we find that the volume of 1 gram of water at 14°, weighed in air with brass weights, is 1.0018 c.c. The flask therefore contained $(501.65 \times 1.0018) = 502.6$ c.c.

The flask may be used with application of the necessary correction, but it is more convenient to make a new graduation at the correct place. The position of this mark is

found as follows:—Calculate the weight of water that will fill the flask to the correct graduation mark (in the above example, $500 \times 0.9982 = 499.1$ grams of water at 14°). Place the calculated weight together with the tare of the flask on the balance-pan and adjust the amount of water in the flask until the total weight of the flask and water is found to be correct.

Etching a line on glass.—A new line should then be etched on the glass at the correct position by means of hydrofluoric acid in the following manner:—Gum on two strips of paper completely round the tube, leaving only a narrow space between them where the line is to be etched (Fig. 21). Warm cautiously above a flame, and rub with a piece of paraffin wax until the paper is saturated with the melted wax. When it has solidified, remove the wax from the line between the two papers by means of a metal point. Fix a narrow strip of filter paper round this line, and wet the paper with hydrofluoric acid solution. (**Caution.**—Care must be taken that the hydrofluoric acid does not come into contact with the skin, since it causes later a particularly painful sore.)

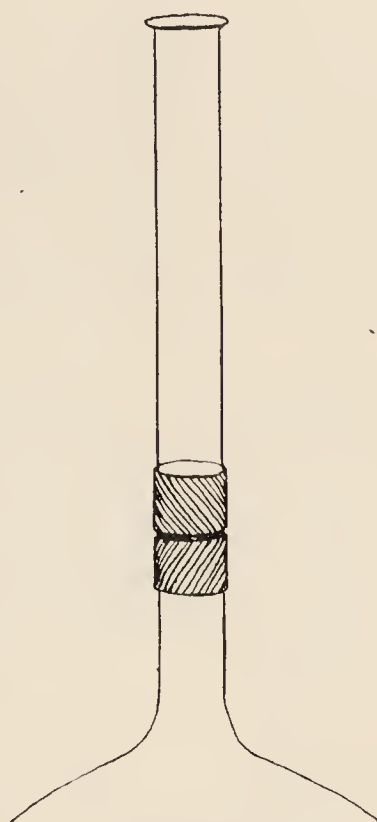


FIG. 21.

After about ten minutes, wash off the hydrofluoric acid and remove a small portion of the paper and wax to ascertain if the glass is sufficiently etched. If the etching is insufficient, re-wax and repeat the process, but allow more time for the etching action.

The permissible errors in graduated flasks are as follows:—

100 c.c. ± 0.05 c.c.	
250 c.c. ± 0.1 c.c.	

500 c.c. ± 0.15 c.c.
1000 c.c. ± 0.2 c.c.

USE AND STANDARDISATION OF A PIPETTE.

The pipette should first be examined to make sure that it is capable of being made an instrument of precision. The narrow tubes should not be above 3 mm. internal diameter

for a 10 c.c. pipette, or 5 mm. for larger sized pipettes. The shoulder should slope gradually to the bulb, as liquid is likely to be retained in the corner if it is badly shaped. A pipette will not deliver constant amounts if it discharges too quickly. The time of outflow must be about twenty seconds for a 10 c.c. pipette, thirty seconds for a 25 c.c. pipette, thirty-five seconds for a 50 c.c. pipette, and forty-five seconds for a 100 c.c. pipette. If the time of outflow is shorter, the aperture may be reduced by heating the jet carefully in a flame until of the desired size. This method of adjustment, however, results in a sudden constriction at the jet, which is much less satisfactory than a gradual taper.



FIG. 22.
A Pipette.

A pipette will not deliver a definite volume unless it is used in a specified manner, and it must be used in the same manner as that adopted during standardisation, viz. :—

1. The pipette must be absolutely clean (see p. 37). Any sign of drops on the surface of the glass indicates that the pipette is not clean.
2. The pipette must be held more or less vertically, with the tip in contact with the side of the receiving vessel.
3. After the continuous discharge, the pipette must be allowed to drain for fifteen seconds, after which the tip of the pipette is drawn along the wet surface of the vessel. A small portion of the liquid always remains in the jet of the pipette, but this should not be expelled.

Standardisation.—Find the weight of an empty weighing-bottle or a small flask, which need not be dried inside. The permissible error in a pipette should not exceed one in a thousand, and in the case of a 10 c.c. pipette the weighing should be accurate to the nearest centigram, *i.e.* to 0.005 gram.

Fill the pipette to the mark with distilled water,¹ run the contents into the weighing-bottle, and re-weigh.

Bottle + water	= 35.215 grams.
Tare of weighing-bottle	= 25.170 „
Weight of water	= 10.045 „

Find the temperature of the water and, with the help of the table on p. 37, calculate the volume of the observed weight of water. If the error in a 10 c.c. pipette is not more than ± 0.01 c.c., the pipette is sufficiently accurate. If the error is greater than this, the pipette must be corrected in the following manner.

A rough estimate as to how far to place the new mark from the old graduation may be obtained by noting how far the water sinks in the narrow tube when one drop is run out of the pipette. One drop of water weighs, roughly, about 0.05 gram. Gum a strip of paper along the pipette and make a mark where it is thought the graduation should be.

Weigh the amount delivered by the pipette with this new graduation, and calculate the volume to which this corresponds. If this is not quite correct, it will serve as a guide to the exact position. When it is certain (by a repetition of the weighing) that a mark on the paper is the correct position for the graduation, a line should be etched on the glass at this place. Before removing the paper with the graduation mark, wash off the etching solution and examine a small portion of the line to be sure that it is properly etched. The permissible errors in pipettes intended for accurate work are as follows:—

10 c.c. ± 0.01 c.c.	50 c.c. ± 0.04 c.c.
25 c.c. ± 0.02 c.c.	100 c.c. ± 0.06 c.c.

¹ Unless the tip of the forefinger that is placed on the upper end of a pipette is smooth and *slightly* moist, it may be found impossible to manipulate the instrument with ease and certainty. If the finger-tip is rough, rub it with pumice; and, immediately before using a pipette, moisten the finger-tip with the lips or tongue and rub the finger and thumb together for a moment.

USE OF A BURETTE.

A burette is usually graduated in tenths of a cubic centimetre. It is fitted at the lower end with a glass tap or with a rubber tube and clip, so that the flow of liquid may be regulated and stopped as desired (Fig. 23). A glass tap must be used with potassium permanganate and iodine solutions, since these attack rubber. In order that the measurements with a burette may be accurate, attention must be paid to the following points:—



FIG. 23.

- (1) The burette must be clean (see p. 37).
- (2) The tap must be lubricated with a mere trace of a suitable lubricant. (Vaseline, or a mixture of vaseline and resin cerate will be found satisfactory.) The tap must not leak.
- (3) The burette must be clamped *vertically*, and at a convenient height above the bench. As a rule it is best to adjust the burette so that the tip of the jet is about half an inch above the top of the receiving vessel.
- (4) Sufficient time must be allowed for draining before the burette reading is taken. To prevent serious error due to neglect of this, the delivery jet must be of such a size that the time of outflow of water from the zero mark to the lowest graduation is about ninety seconds for a 30 c.c. burette and one hundred and fifty seconds for a 50 c.c. burette, with the tap fully open. If the burette discharges more quickly, the jet may be constricted by drawing it out in a flame.
- (5) The level of a liquid in a burette is read by noting the graduation opposite the lower boundary of the dark portion of the meniscus (except with opaque solutions as explained on p. 78), and an accurate reading requires (*a*) suitable illumination of the meniscus (*b*) avoidance of parallax error. A simple method of illuminating the meniscus is to hold a

white card behind the burette, as shown at M in Fig. 24. The eye must be at the same level as the meniscus; it is evident that readings from positions A or B will be incorrect.

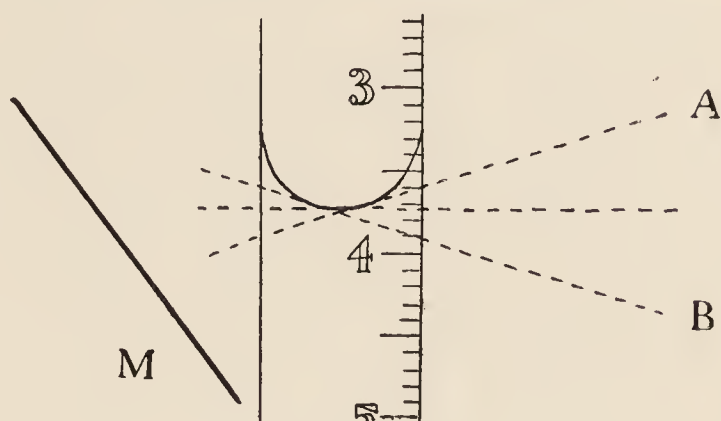


FIG. 24.

A more satisfactory device, which gives good meniscus illumination and completely eliminates parallax error, is shown in Fig. 25.¹ A piece of white celluloid, measuring about 3 inches by

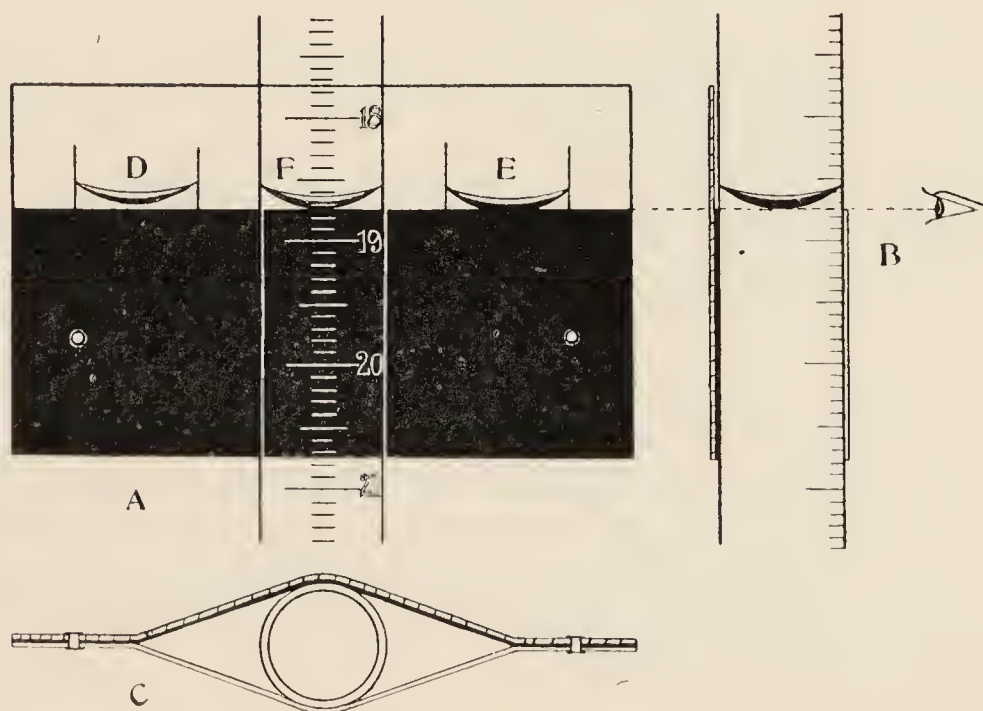


FIG. 25.

$1\frac{1}{2}$ inches, has two-thirds of its area blackened, as shown in diagram A; exactly covering the black area and fixed to it by means of two eyelets is a strip of transparent celluloid. The device is

¹ This device may be obtained from Mr A. H. Baird, Lothian Street, Edinburgh.

slipped over the burette (as shown in diagram C) and will remain in any desired position. A burette reading is made as follows:—

The device is placed on the burette so that the upper margin of the black area is just below the meniscus. (The meniscus then appears as a black crescent with a very sharp lower outline.) The eye is brought into the position such that the upper edge of the transparent celluloid (in front of the burette) and the upper margin of the black area (behind the burette) are seen as one coincident line, and the device is gradually raised until this line forms a tangent to the black crescent of the meniscus. This is shown in diagram B and also at F. The slightest movement of the eye throws the front and back margins of the device out of alignment, while the slightest movement of the device itself causes the meniscus to appear above or below the coincident margins, as shown at D and E. After adjusting the device in this manner, the burette reading is obtained, without further reference to the meniscus, by noting the position on the burette of the upper margin of the transparent celluloid. It is possible to read to the nearest 0.01 c.c., especially with the aid of a pocket lens.

Another device is found in the Schellbach burette (Fig. 26) which has a broad, white band along the back and a narrow (usually blue) band in the middle of the white one. The error due to parallax is lessened, but is not completely eliminated, by this device.

When washing out a burette, the open end should be closed with a cork—not with the finger because this makes the glass greasy; or the burette may be washed by running in some water and tilting the tube up and down. After washing a burette it should be drained as completely as possible, and, before filling it with a solution, it must be rinsed out with a little of the solution in order to remove the water still adhering to the wall. The solution should

be poured into the burette through a small, dry funnel. The funnel must be removed from the burette and the air expelled from the jet before the initial reading is taken.

In titrations it is often possible to judge the end-point with an accuracy of about 0.01 c.c. To enable this to be done and to avoid over-stepping the end-point, the solution in the burette must be cautiously added in fractions of a drop at a time, when near the end-point. Fractional drops may be removed from the jet of the burette with a stirring-rod, or by bringing the side of the receiving vessel into contact with the jet. The size of the drops that form at the jet depends mainly on the external diameter of the jet, and if a fine jet is made slightly greasy by drawing the fingers over it, drops of less than 0.02 c.c. may be obtained.



FIG. 26.

Calibration of a Burette.

A burette that is to be used for accurate work must be tested or calibrated, unless it is a verified instrument. The calibration of a burette demands very careful manipulation on the part of the operator, who must have had previous experience in handling the instrument and must know how to use it properly.

Procedure.—Clean the burette very carefully. Lubricate the tap and make sure that it does not leak. Clamp the burette *vertically* at a convenient height above the bench. Fill the burette with distilled water, the temperature of which is the same as that of the room. (Ascertain this temperature which, preferably, should be near 15°.) Expel air from the jet of the burette. With the help of the device shown in Fig. 25, carefully adjust the level of the water to the zero graduation of the burette. Remove any drop adhering to the jet by bringing the jet into contact with the side of a beaker.

Now run the water slowly (see par. 4, p. 42) from the burette into a small, weighed flask¹ until the level reaches

¹ Weigh to the nearest centigram, *i.e.* to ± 0.005 gram.

(approximately) the 5 c.c. graduation. Remove any drop adhering to the jet by bringing the inside of the receiving flask into contact with the jet. Allow the burette to drain for thirty seconds and then read it carefully. Find the weight of the water delivered and calculate its volume with the help of the data on p. 37.

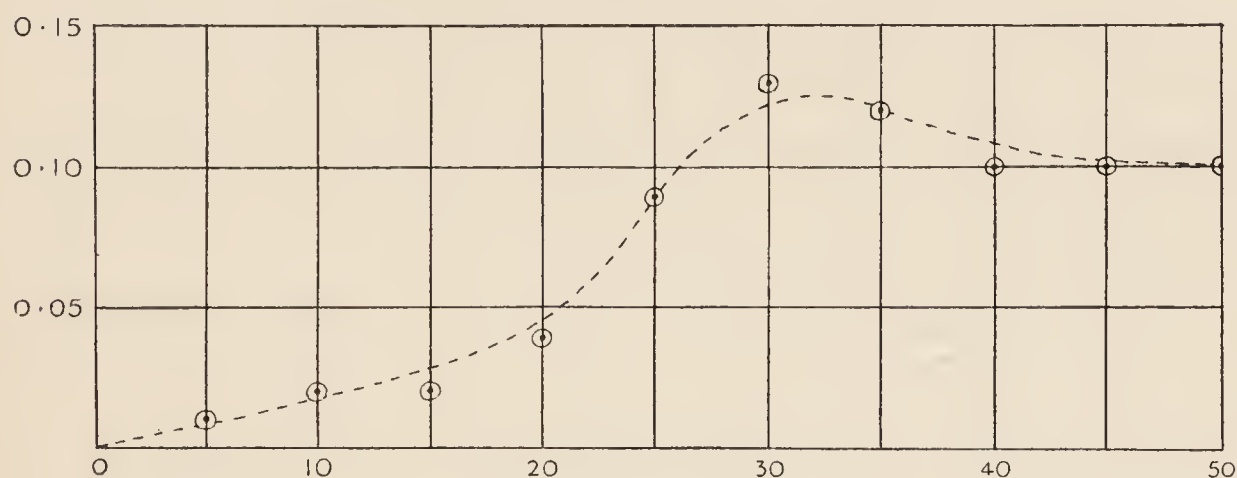
Fill the burette to the zero mark again and run off approximately 10 c.c. of water. Read the burette after it has drained for thirty seconds, weigh the water delivered, and calculate its volume. In the same manner, starting from zero each time, ascertain the volume of water delivered from 0–15 c.c., 0–20 c.c., 0–25 c.c., and so on, until finally the burette has been tested at approximately each 5 c.c. graduation interval.

Repeat the whole calibration and tabulate the results as shown below. In the example given, the temperature was 15°, and from the table on p. 37 it is found that the volume, at 15°, of 1 gram of water is 1.0019 c.c. Duplicate corrections at any point tested should not differ by more than 0.01 c.c.

Burette reading.	Weight of water delivered.	True volume.	Correction at each reading.
5.04	5.035	5.05	+ 0.01
10.05	10.055	10.07	+ 0.02
15.08	15.075	15.10	+ 0.02
20.06	20.060	20.10	+ 0.04
25.07	25.115	25.16	+ 0.09
30.10	30.170	30.23	+ 0.13
35.06	35.110	35.18	+ 0.12
40.03	40.055	40.13	+ 0.10
45.08	45.095	45.18	+ 0.10
49.98	49.985	50.08	+ 0.10

Care must be taken to avoid mistakes in the sign (plus or minus) of the corrections. A plus correction must be added to, and a minus correction must be subtracted from, the corresponding burette reading in order to obtain the true volume. By plotting the corrections against the corresponding burette readings, a curve of corrections is obtained. Since the error in reading a burette is about 0.01 c.c., the corrections themselves may involve an equal

error, and a “smoothed” curve is therefore drawn through the points as shown in the diagram. The correction at any burette reading may be obtained at once from the curve. For example, if the liquid were run out from 3.01 c.c. to 27.46 c.c., the corrected readings are $3.01 + 0.01 = 3.02$ c.c. and $27.46 + 0.11 = 27.57$ c.c., and the volume delivered was $27.57 - 3.02 = 24.55$ c.c. If no corrections were made it would be 24.45 c.c.—a difference of 0.4 per cent.¹



It is advisable to reject a burette if there are serious errors, and particularly if there are marked irregularities in it. A 50 c.c. burette may be regarded as satisfactory if the error at any point does not exceed ± 0.05 c.c., provided that the difference between the errors at any two points does not exceed 0.05 c.c. For example, an error of $+0.04$ at one point must not be accompanied by an error of -0.02 at another point.

GENERAL NOTES ON THE PREPARATION OF STANDARD SOLUTIONS.

For obvious reasons it is desirable that a standard solution should not alter in concentration on keeping; volatile or unstable substances are therefore to be avoided if possible.

Solutions more concentrated than *normal* are rarely

¹ This burette (of Continental origin) appears to be graduated in terms of Mohr's unit and not in millilitres, since, at 15° , it delivers *grams* of water (approximately); compare the first and second columns of the calibration table.

required in analytical work. More dilute solutions may be prepared with accuracy from a standard N solution by using a *standardised* pipette and flask.

As a general rule, the solution or solid from which the standard solution is to be prepared is washed into the standard flask through a funnel with a short stem. The flask must of course be clean, but it is unnecessary to dry it. Standard flasks should not be heated. If it is necessary to apply heat in the preparation of the solution, this operation should be performed in a beaker, and the solution then cooled before pouring it into the flask. If the solution is prepared in a beaker or other vessel, the volume of liquid must be such that ample wash-water may subsequently be used without exceeding the volume of the standard flask.

Before making up to the mark, the contents of the flask must be sufficiently mixed, to ensure that there is no considerable difference in concentration between the top and bottom layers. To accomplish this, the contents of the flask are mixed by rotation when the level is a little below the neck. If this is not done, an error is introduced by the change of volume that occurs when mixing takes place.

The solution must be at or near 15° before making it up to the graduation mark. Attention to this is specially necessary if the process of solution or dilution is accompanied by a considerable heat evolution, *e.g.* with sulphuric acid or sodium hydroxide. In that case it is advisable to dilute almost to the full amount and cool by running tap-water over the flask. The final addition of water to bring the level up to the graduation mark is most easily made from a wash-bottle with a fine jet.

Before pouring any of the liquid out of the flask, the stopper should be firmly inserted and the contents thoroughly mixed by inverting the flask six times at least. This must on no account be neglected, otherwise serious errors will be introduced.

The solution is best stored in a stoppered bottle. The bottle must be rinsed out two or three times with small quantities of the solution, the portions used for rinsing being rejected. The bottle should be clearly labelled with

the name of the solution, the exact concentration, and the date of standardisation. If there is more than one common method for the standardisation of the solution, the label should indicate which method was adopted.

Hydrochloric Acid
1.017N (by calcspar)
29/3/28

When a bottle of standard solution has been set aside for some time, drops of liquid will be found to have condensed on the upper part of the bottle. As these drops differ in concentration from the main portion of the solution it is always advisable to shake the bottle before use.

Preparation of a Standard Solution of a desired Concentration.

The usual practice in the preparation of a standard solution is to make the solution of approximately the required concentration, then to determine the exact value, and use this value as a "factor" in the calculations. It is sometimes necessary, however, to prepare a solution which is, for example, *exactly* normal, or decinormal, and the following is an illustration of a method that may be used.

Preparation of an exactly Normal Solution.—In preparing the solution it is better to make it somewhat too concentrated at first rather than too dilute, as it is an easier matter to alter the concentration by addition of water than by addition of weighed quantities of the solute.

Example.—A solution of sodium carbonate was found by titration to be 1.045N. It is clear that 1000 c.c. of the solution contains 1.045 equivalents, and that it could be made exactly normal by increasing the volume to 1045 c.c. If 45 c.c. of water were added to 1 litre of the solution, there would then be 1.045 equivalents in *about* 1045 c.c.¹

¹ Addition of 45 c.c. of water will not give exactly 1045 c.c. The volume obtained when a solution is diluted with water is slightly less than the sum of the volumes taken, but the difference is so small that it may be neglected except with concentrated solutions.

The volume of the solution should be determined by means of a measuring cylinder; suppose, for example, the volume of the sodium carbonate solution was found to be 440 c.c. The amount of water to be added is then

$$\frac{440}{1000} \times 45 = 19.8 \text{ c.c.}$$

The 19.8 c.c. of water is run out from a burette into the solution in the measuring cylinder. (Take care to add too little rather than too much water.) The solution is poured back into the bottle, shaken, and again titrated with standard acid. If it is still too concentrated, again add the calculated amount of water and again titrate. After the second adjustment the solution should be of the required concentration; if not, continue the process. After adding any water, always return the solution to the bottle and shake it before titrating it with the acid.

Acidimetry and Alkalimetry

THE determination of the concentration of acids by means of standard alkali solutions is known as acidimetry, and the reverse process as alkalimetry. The choice of acids and alkalis for standard solutions is partly a matter of convenience, but for certain purposes the choice is restricted, *e.g.* a standard sodium carbonate solution cannot be used instead of a standard sodium hydroxide solution for the determination of acetic acid (see p. 53).

Standard Acids.—The only acids in common use are hydrochloric and sulphuric acids. The preparation of normal solutions of each, with various methods of standardisation, will be found below; more dilute standard solutions are best prepared by dilution of the normal solution.

For almost all purposes, it is immaterial which acid is used, but probably hydrochloric acid has the wider range of utility. Normal hydrochloric acid is quite stable and has no tendency to lose the free acid; indeed, if exposed to the air, it becomes more concentrated.

Standard Alkalis.—Sodium hydroxide, sodium carbonate, and barium hydroxide are all used for standard solutions, and each has advantages over the others for special purposes. The selection of an indicator is of special importance in connection with standard alkalis; and it is essential that in standardising and in subsequently using a standard alkali one and the same indicator should be used.

NOTES ON THE USE OF INDICATORS.

The indicators used in acidimetry and alkalimetry are sometimes said to show when a solution is neutral, but this is only approximately true.

A neutral solution is one in which, as in ideally pure

water, the concentrations of the acid ion (hydrion) H^+ and the alkaline ion (hydroxidion) OH^- are equal, and are each approximately 1×10^{-7} normal (0.0000001 N). If the concentration of hydrion is greater than that of hydroxidion, the solution is acid; if it is less than that of hydroxidion, the solution is alkaline. In pure water and in all dilute aqueous solutions, whether acid, neutral, or alkaline, the product of the concentrations of hydrion and hydroxidion is constant and equal to 1×10^{-14} . Accordingly, if the hydrion concentration is, for example, 10^{-5}N , the hydroxidion concentration is 10^{-9}N , and the solution is acid; and if the hydrion concentration is 10^{-8}N , the hydroxidion concentration is 10^{-6}N , and the solution is alkaline.

Indicators for acid and alkali are, strictly speaking, substances that exhibit a conspicuous change of colour when the concentration of hydrion (or hydroxidion) falls to a certain value which, in general, is not that of absolute neutrality (*i.e.* 10^{-7}N) and which differs, in fact, with different indicators.

Methyl orange, for example, is red in acid solution and becomes yellow when the hydrion concentration is reduced to about 10^{-5}N , *i.e.* before the neutral point is reached and when the concentration of hydrion is still 100 times greater than in a neutral solution. Phenolphthalein is without colour in an acid solution and also at the neutral point, and becomes pink only when the hydrion concentration is reduced to about 10^{-9}N , *i.e.* when the hydroxidion concentration is about 10^{-5}N , or 100 times greater than at the neutral point. The "change-points" of methyl red and litmus lie nearer the true neutral point.

It should also be noted that when equivalent quantities of an acid and base are mixed, the resulting salt solution is not absolutely neutral except in the case of a *strong acid and a strong base*, which form a salt that is not hydrolysed. If a *weak acid and a strong base*, such as acetic acid and sodium hydroxide, are mixed in equivalent quantities, the resulting solution is not neutral but alkaline on account of the hydrolysis of the sodium acetate, and a slight excess of acid must be added to produce a neutral solution. Similarly, equivalent quantities of a *weak base and a strong acid* yield an acid solution.

These various facts, however, do not seriously impair the accuracy of the results in ordinary volumetric analysis provided suitable indicators are chosen, in accordance with the following instructions:—

- (1) For the titration of a strong acid with a strong base (free from carbonate) and *vice versa*, any indicator may be used if the concentration of the standard solution is not less than fifth-normal. With more dilute solutions use methyl red or phenolphthalein.
- (2) For the titration of a weak acid with a strong base use phenolphthalein.
- (3) For the titration of a weak base with a strong acid use methyl red.
- (4) For the titration of salts of very weak acids with strong acids use methyl orange. Methyl red or litmus may be used for carbonates or sulphides if the titration is carried out at the boiling-point of the solution.

The titration of a weak acid with a weak base, *e.g.* acetic acid with ammonia, is avoided in practice, because no indicator used in the ordinary way will give a sharp end-point; and it is not possible to titrate salts of very weak acids with weak acids, *e.g.* sodium carbonate with acetic acid.

Further particulars as to the uses of these indicators are given below.

Methyl Orange.—Very weak acids have little or no effect on this indicator and it is therefore specially adapted for the titration, with strong acids, of salts of very weak acids such as carbonates, bicarbonates, sulphides, silicates, borates, and arsenites. As carbonic acid is not entirely without influence on methyl orange, it is advisable in the titration of carbonates to expel most of the carbon dioxide when near the neutral point by warming and shaking the solution; the solution must be cooled before completing the titration, as the titration of hot solutions gives somewhat inaccurate results when using methyl orange.

Methyl orange cannot be used for the titration of weak

acids. It may be used for ammonia, but methyl red gives a much sharper end-point.

Methyl Red.—This is the best indicator for the titration of ammonia or for solutions containing ammonium salts. It is more sensitive and gives a much sharper end-point than methyl orange with very dilute solutions of strong acids and bases. It is useless for weak acids like acetic acid. It may be used for the titration of soluble carbonates if the solution is heated to the boiling-point. Methyl red is, however, much less sensitive to carbonic acid than litmus or phenolphthalein, and the amount of carbonate present in an ordinary solution of sodium hydroxide is almost without influence on the indicator.

Phenolphthalein.—This indicator should be used only with strong bases free from carbonate. It is chiefly valuable for the titration of weak acids. Organic acids insoluble in water can be titrated in aqueous alcohol solutions with this indicator. Phenolphthalein must not be used for ammonia or in presence of ammonium salts. With carbonates of the alkalis it indicates “neutrality” roughly at the stage of bicarbonate.

Litmus.—This indicator is often unsatisfactory in accurate work unless a purified product, such as azolitmin, can be obtained. It may be used for strong acids and bases, but is inaccurate if the alkali contains carbonate. It is fairly satisfactory for ammonia, but must not be used for weak acids. It may also be used in the titration of soluble carbonates, bicarbonates, and sulphides, provided the carbon dioxide or hydrogen sulphide is expelled by boiling during the operation.

In connection with the use of the above indicators, it should be noted that ordinary sodium hydroxide invariably contains some carbonate, and if a solution of sodium hydroxide is intended for use with more than one indicator, it should be standardised separately, using each indicator, and the appropriate value for the normality, corresponding to each indicator, used in subsequent work.

Amount of Indicator to be Used.

The preparation of indicator solutions is described in the Appendix (p. 418). It is important to note that *they are much more dilute than the solutions usually recommended*. It is a common mistake to use too much indicator, and if only *one* drop of a concentrated solution is required, the addition of "a few drops" represents a large excess. The concentrations recommended in the Appendix are so chosen that approximately 1 c.c. of the indicator solution is required for each 50 c.c. of liquid present at the end of the titration. One c.c. of the indicator can be measured with sufficient accuracy by means of a pipette (Fig. 27) roughly graduated to deliver this quantity.

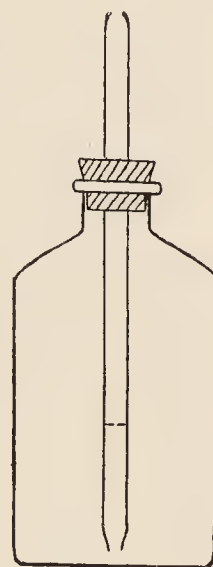


FIG. 27.

NORMAL HYDROCHLORIC ACID.¹

(36.47 grams HCl per litre.)

Standard hydrochloric acid may be prepared (1) by diluting a known volume or weight of "constant boiling-point" acid (see p. 60), or (2) by preparing a solution of approximately the desired concentration and then standardising it by one of the methods given below.

Commercial concentrated hydrochloric acid is usually about 10N. Prepare an approximately normal solution of the acid by diluting 100 c.c. of the concentrated acid in a measuring cylinder to a litre. Transfer the solution to a bottle and *mix thoroughly* by inverting the bottle several times. Standardise the solution by the following methods:— (1) By means of calcspar; (2) by means of (a) sodium carbonate decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, or (b) anhydrous sodium carbonate.

¹ The preparation of *normal* solutions of acids and alkalis is described. If *semi-normal* solutions are required, use half the quantities of concentrated hydrochloric acid, sodium hydroxide, etc., prescribed for normal solutions; and in standardising semi-normal solutions use half the quantities of calcspar, sodium carbonate, etc., prescribed for normal solutions.

Standardisation of Hydrochloric Acid by means of Calcspar.

First method.—Select a good piece of calcspar weighing from 3 to 5 grams. Place it in a beaker and cover with dilute hydrochloric acid for two or three minutes to remove the fine powder on its surface. Wash the calcspar thoroughly with water and dry it with filter paper.

Clean and dry a small (100 c.c.) beaker or conical flask. Place the piece of calcspar in the vessel and heat the vessel and contents in the steam-oven for one hour. Allow to cool in the balance-room for half an hour, and then find the weight of the vessel plus calcspar. With a pipette measure into the beaker or flask 25 c.c. of the acid to be standardised. If a beaker is used, cover it immediately with a watch-glass; if a flask is used, place a bulb in the mouth (Fig. 10, p. 23). Set aside for several hours or overnight.

Wash down the sides and cover of the vessel, add 1 c.c. of methyl orange, and warm on the steam-bath until the solution becomes neutral (yellow colour).

Pour off the calcium chloride solution, and wash thoroughly by decantation, care being taken that there is no loss of any small pieces of the spar that may have become detached from the main portion. Drain off as much of the water as possible and dry the vessel and contents (with the cover removed) in the steam-oven for one hour. Cool in the balance-room for half an hour, and weigh.

From the loss of weight, calculate the concentration of the hydrochloric acid.

Example :—

Original weight of beaker and spar = 16.5124 grams

Final " " " = 15.2514 "

Weight of CaCO_3 dissolved by 25 c.c. = 1.2610 "

Therefore 1000 c.c. of the acid will dissolve 50.44 grams CaCO_3 .

But 1000 c.c. normal acid will dissolve 50.03 grams CaCO_3 .

Therefore the given acid is $\frac{50.44}{50.03} = 1.008$ normal.

Note.—The solubility of ordinary glass in water and in acid and alkaline solutions occasions an appreciable error in this and similar experiments in acidimetry. The error is considerable in the case of glass that has not been in use for some time. To minimise the error, the flask or beaker used in the above experiment should be “steamed,” *i.e.* steam should be blown through it for ten minutes before finally rinsing it out for use. With resistance-glass vessels the error is practically negligible.

Alternative method.—Clean and dry a small beaker of about 100 c.c. capacity, together with a watch-glass to cover it. Weigh the beaker and cover, and then weigh in it from 1 to 1.2 grams of powdered calcspar, *e.g.*,

Beaker, watch-glass and calcspar	=	17.009 grams
Tare of beaker and watch-glass	=	15.998 „
Weight of calcspar	=	1.011 „

Cover the calcspar with water and run in from a pipette 25 c.c. of the hydrochloric acid, keeping the beaker covered as much as possible to prevent loss during the effervescence. After a few minutes warm the solution *gently* to complete the reaction and to expel most of the carbon dioxide.

Wash down the sides of the beaker and the cover-glass. Titrate the excess acid with an alkali solution, using 1 c.c. of methyl orange as indicator. It is not necessary to know the concentration of this alkali, but its titration value against the acid must be known. The amount of unused acid is then calculated. Subtraction of this from the 25 c.c. taken gives the volume neutralised by the calcspar, and from this the concentration of the acid is calculated.

Example.—1.011 grams of calcspar were dissolved in 25 c.c. of hydrochloric acid solution and 6.02 c.c. of alkali were used in the “back titration,” using methyl orange as indicator. Twenty-five c.c. of this alkali neutralised, using the same indicator, 23.94 c.c. of the acid. The 6.02 c.c. of alkali correspond, therefore, to $\left(\frac{23.94}{25} \times 6.02\right)$ c.c. = 5.76 c.c. of acid.

Therefore 1.011 grams of CaCO_3 neutralised $(25 - 5.76)$ = 19.24 c.c. of acid. The hydrochloric acid is 1.050N.

**Standardisation of Hydrochloric Acid by means of
Sodium Carbonate Crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.**

The sodium carbonate must be free from sulphate and chloride, and crystals that show any traces of efflorescence must be rejected.

Place about 10 grams of selected crystals in a weighing-bottle and weigh to the nearest milligram. Transfer 3 to 3.5 grams to a 300 c.c. conical flask and reweigh the bottle to find the weight of sodium carbonate taken. Dissolve the crystals in about 50 c.c. of water, add 2 c.c. of methyl orange, and titrate with the hydrochloric acid. Warm and shake the solution when near the neutral point to expel most of the carbon dioxide, but cool again to room temperature before finishing the titration. Calculate the concentration of the acid. Repeat the experiment until results agreeing to within 2 in 1000 are obtained.

Alternative method.—To a weighed quantity of the crystals add a measured volume of hydrochloric acid, taking the acid in slight excess (3 to 3.2 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and 25 c.c. of approximately N acid are convenient quantities). Boil the solution for a minute to expel the carbon dioxide, and titrate the excess acid with an alkali solution, using methyl orange or methyl red as indicator. The method of calculation is explained for a similar case on p. 57. The end-point obtained by this method is sharper than in the direct titration method, the difference being more noticeable with decinormal than with normal solutions.

**Standardisation of Hydrochloric Acid by means of
Anhydrous Sodium Carbonate.**

The sodium carbonate required for this purpose must answer the following tests:—

- (1) Dissolve 1 gram in 25 c.c. of distilled water; the solution should be perfectly clear. Add dilute nitric acid (free from chloride) in slight excess and then a few drops of silver nitrate solution. No turbidity (or only a *very faint* opalescence) should appear.

- (2) Dissolve 1 gram in 25 c.c. of distilled water. Add sufficient dilute hydrochloric acid (about 10 c.c.) to make the solution *faintly* acid. Then add about 1 c.c. of barium chloride solution, heat until boiling, and set aside until cold. No trace of barium sulphate should be precipitated.

If the sodium carbonate is free from chloride and sulphate, and from insoluble impurities, it must next be dried. Heat 3 to 4 grams in a small porcelain basin (a platinum crucible is preferable) over a moderate Bunsen flame, with frequent stirring, for twenty minutes; regulate the flame so that the bottom of the crucible is barely red hot; the substance must not fuse or form into hard lumps. Allow to cool partially, and transfer while still warm to a clean, dry weighing-bottle.

In order to avoid over-heating the carbonate, the basin or crucible may be heated on a sand-bath to 300° for thirty minutes, with frequent stirring.

When the weighing-bottle is perfectly cold, weigh it accurately, shake out from 1 to 1.3 gram of the carbonate into a suitable beaker or conical flask, and weigh again. Shake out a second quantity into another beaker, and again weigh.

Dissolve each portion of carbonate in about 30 c.c. of water, add 1 c.c. of methyl orange, and titrate with the hydrochloric acid. Calculate the concentration of the acid as follows:—

1.251 grams Na_2CO_3 required 23.52 c.c. acid. Therefore 1 litre of acid is equivalent to $\frac{1.251 \times 1000}{23.52} = 53.17$ grams Na_2CO_3 . But 1 litre of normal acid is equivalent to 53.0 grams Na_2CO_3 . Therefore the acid is $\frac{53.17}{53.0} = 1.003\text{N}$.

The two results should agree to about 2 in 1000.

Sodium bicarbonate, free from chloride and sulphate and insoluble impurities, may be used for the preparation of the normal carbonate. For this purpose, water and carbon dioxide are driven off by heating to a moderate temperature, as in the case of sodium carbonate, in a platinum crucible (or a porcelain basin) for thirty minutes, with frequent stirring. The normal carbonate is used as described above.

**Preparation of Standard Hydrochloric Acid Solution
from the Constant Boiling-Point Acid.**

When a solution of hydrochloric acid of any arbitrary concentration is distilled, the distillate has not, in general, the same composition as the residue. The boiling-point rises as the distillation proceeds and tends towards a maximum. When this point is reached, the remainder of the solution distils unchanged at a constant boiling-point, and the distillate and residue have then a definite composition. The composition varies with the pressure, but the variation caused by any ordinary barometric change is so small that it may be neglected even for exact work.

With the help of a specific gravity bulb, make up 600 c.c. of hydrochloric acid solution of as near 1.10 sp. gr. as possible. Boil this solution in a narrow-mouthed flask until its volume is reduced to about 200 c.c. (The evaporation must not be done in an open vessel, as errors are introduced if air has access to the surface of the liquid.) Cool the residue.

This constant boiling-point acid contains 20.24 per cent. by weight of hydrochloric acid, and 180.2 grams made up to one litre therefore give a normal solution. The constant boiling acid is neither hygroscopic nor noticeably volatile, and may be weighed in a small tared flask. The final adjustment of the exact weight required may be made with the help of a tube drawn out to a fine capillary.

If there is any doubt as to the purity of the original acid, it is better to condense the vapour after two-thirds have been boiled off and use this distillate instead of the residue.

NORMAL SULPHURIC ACID.

(49.04 grams H_2SO_4 per litre.)

Dilute 30 c.c. of ordinary concentrated sulphuric acid by running it slowly into 150 to 200 c.c. of cold water contained in a flask. (**Caution.**—The acid must be run into the water, not *vice versa*.) After cooling the solution under the tap, pour it into a measuring cylinder and dilute to a litre. The solution prepared in this way will be slightly above normal; the exact concentration must be found by standardisation.

Standardisation.—Sulphuric acid may be standardised in exactly the same manner as hydrochloric acid with weighed quantities of sodium carbonate (see p. 58).

Calcspar cannot be used as a standard for sulphuric acid on account of the insolubility of calcium sulphate.

Sulphuric acid is often standardised gravimetrically by precipitation as barium sulphate. Ten c.c. of a normal solution or 50 c.c. of a decinormal solution is sufficient for each gravimetric determination. The details of the gravimetric method are given on p. 169.

NORMAL SODIUM HYDROXIDE.

(40.01 *grams NaOH per litre.*)

Sodium hydroxide is very deliquescent, and the commercial “sticks” contain varying amounts of carbonate. For most purposes, the solution made from ordinary “white sticks” may be used, but when a “carbonate-free” hydroxide is required the solution must be prepared by one of the special methods given below.

Weigh about 42 grams of sodium hydroxide on a rough balance. Drop the sticks without delay into a bottle containing about 800 c.c. of water. Close the bottle with an ordinary cork or a rubber stopper, and shake gently during the process of solution, otherwise the heat evolved may cause the bottle to crack. Dilute the solution to about 1 litre. (A mark should have been made on the bottle to show this volume.) Allow the solution to cool before standardising it.

Standardisation.

This solution must be standardised, and the method adopted depends on the use to be made of the solution. If it is to be used solely in conjunction with standard acid, *e.g.* for the back-titration in ammonia determinations, it must be standardised by titration against standard acid with methyl orange or methyl red as indicator.

If the sodium hydroxide is to be used for the determination of weak acids, it must be standardised with standard acid, potassium tetroxalate, oxalic acid, or succinic acid, using phenolphthalein as indicator.

Standardisation with Normal Acid.—Titrate 25 c.c. of normal acid with the sodium hydroxide, using methyl red as indicator. Repeat the titration, using phenolphthalein and methyl orange as indicators. The results usually differ slightly and the normality should therefore be calculated separately for each indicator.

Standardisation with Potassium Tetroxalate.—Weigh accurately on a watch-glass about 2 grams of potassium tetroxalate. Wash it into a conical flask, add about 50 c.c. of water and 2 c.c. of phenolphthalein solution, and titrate slowly with the sodium hydroxide. The tetroxalate is not very soluble in water, but it dissolves completely as the titration proceeds and the end-point is well defined.

The formula of potassium tetroxalate is $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$. It has three replaceable H atoms in the molecule, so that the gram-equivalent is 84.7 (one-third of the molar weight).

Example of Calculation.—If 28.20 c.c. of a sodium hydroxide solution neutralises 2.178 grams of potassium tetroxalate—

1 litre will neutralise $\frac{2.178 \times 1000}{28.20}$ grams. But 1 litre of *normal* sodium hydroxide solution will neutralise 84.7 grams. Therefore the sodium hydroxide solution is

$$\frac{2.178 \times 1000}{28.20 \times 84.7} = 0.912\text{N},$$

and contains $40.01 \times 0.912 = 36.49$ grams NaOH per litre.

Repeat the experiment with another weighed quantity of potassium tetroxalate, and calculate the concentration of the sodium hydroxide solution from the result. The experiment should be repeated until results that agree to 2 in 1000 are obtained.

Standardisation with Oxalic or Succinic Acid.—The gram-equivalent of oxalic acid, $(\text{COOH})_2, 2\text{H}_2\text{O}$, is 63.03, and that of succinic acid, $(\text{CH}_2 \cdot \text{COOH})_2$, is 59.03. About 1.5 gram of either acid should therefore be taken for titration against N alkali.

Decinormal Sodium Hydroxide.

Decinormal sodium hydroxide solution may be made up by dilution of the normal solution with recently boiled and cooled water, using a standardised pipette and flask.

A decinormal solution may also be prepared by dissolving 4 grams of sodium hydroxide in about 1 litre of water and standardising by the methods already described.

Preparation of Carbonate-free Sodium Hydroxide.

Sodium hydroxide is often used for the determination of weak acids, with phenolphthalein as indicator. If any carbonate is present, the end-point is not satisfactory. Commercial sodium hydroxide almost invariably contains some carbonate as impurity, and it is therefore preferable to prepare a solution as required from metallic sodium. The following method may be used, except in the rare cases where the presence of alcohol is not permissible.

Cut away the layer of oxide from the surface of a piece of sodium, using alcohol to lubricate the knife. Weigh out approximately 23 grams of the metal and drop it, in small pieces at a time, into about 25 c.c. of ethyl alcohol contained in a porcelain basin. When the reaction becomes sluggish, it can be hastened by the *cautious* addition of a few drops of water. During the reaction protect the solution from atmospheric carbon dioxide by means of a clock-glass over the basin; and, immediately solution is complete, dilute with CO_2 -free water (p. 65) to a litre.

This solution will be almost free from carbonate, but it will only remain so if it is carefully protected from atmospheric carbon dioxide. The apparatus described on p. 64 is convenient for that purpose.

Alternative method. — Dissolve 200 grams of sodium hydroxide in 250 c.c. of water contained in a conical flask. Transfer the solution to a tall, narrow bottle with a rubber stopper fitted with a soda-lime tube, and set the bottle aside for a week or longer until the undissolved sodium carbonate has settled. The clear solution is practically free from carbonate, and is about 15N. To prepare an approximately normal solution, dilute 65 c.c. to 1 litre with CO_2 -free water.

STANDARD BARIUM HYDROXIDE (BARYTA) SOLUTION.

(*N/20 solution contains 7.890 grams $Ba(OH)_2, 8H_2O$ per litre.*)

The titration of acids, using phenolphthalein or methyl red as indicator, is accurate only if made with an alkali free from carbonate. Commercial sodium hydroxide always contains carbonate, and even when a pure solution is prepared

from sodium and water free from carbon dioxide, it soon becomes contaminated with carbonate by exposure to air. Barium and calcium hydroxide solutions, on the other hand, are easily obtained free from carbonate, since the carbonates are nearly insoluble in water (and still less soluble in solutions of the hydroxides), and if protected from carbon dioxide they form convenient and accurate standard solutions for use with the above indicators.

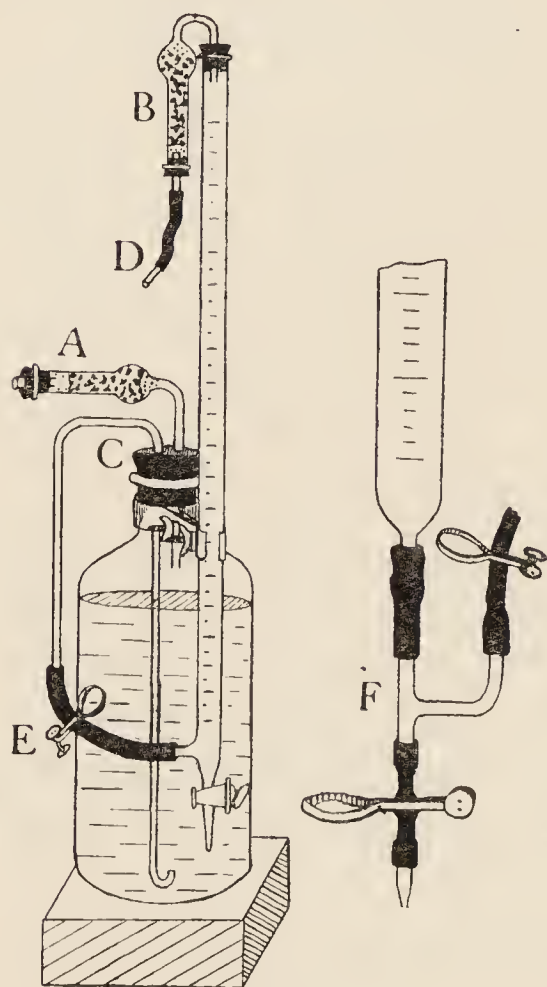


FIG. 28.

Preparation of N/20 Baryta Solution. — Dissolve about 35 grams of barium hydroxide [$Ba(OH)_2, 8H_2O$] and 10 grams of barium chloride in 350 c.c. of boiling water contained in

a flask, then fit the flask with a cork carrying a soda-lime tube, and set aside until cold. The excess of baryta crystallises, and a clear, saturated solution, which is about 0.35 normal, is obtained.

The standard baryta solution must be kept in a bottle which is permanently connected with a burette, atmospheric carbon dioxide being excluded by means of the soda-lime tubes A and B (see Fig. 28). Pour about two litres of water into the bottle (a Winchester quart), and connect it with the burette as shown. Remove the soda-lime tube A and insert, temporarily, a piece of ordinary glass tubing in its place

Attach this tube to the water pump, close the burette tap, and draw a current of air free from carbon dioxide through the burette and bottle for ten minutes. (As the soda-lime tube B is small, more efficient purification of a rapid air-current is secured by attaching temporarily a large soda-lime tower to the tube D.) Replace the soda-lime tube A, lift the cork C, carefully decant the cold baryta solution into the bottle, and replace the cork. Mix the contents of the bottle by drawing a current of CO_2 -free air through the solution, and fill the burette by opening the clip E and applying suction at D. If the solution is slightly turbid owing to a trace of suspended barium carbonate, allow it to stand overnight before drawing it into the burette. The solution should be approximately 0.05 normal, and it may be standardised with pure succinic acid, potassium tetroxalate, or decinormal hydrochloric acid, using phenolphthalein as indicator.

When the burette is not in use, it should be kept filled up above the zero mark, and when used intermittently the first 5 to 10 c.c. run out of the burette are rejected. If a burette with side-tube is not available, an ordinary burette fitted with a T-piece, as shown at F in Fig. 28, is equally convenient. The burette may be fixed in an ordinary clamp, the Winchester resting on the base of the retort stand; or it may be attached to the bottle by means of an Ostwald burette clamp (Fig. 29).

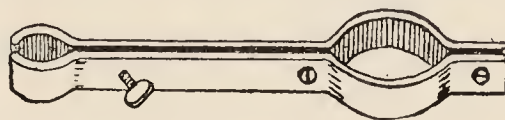


FIG. 29.

STANDARD CALCIUM HYDROXIDE SOLUTION.

(*N/25 solution contains 1.482 grams $\text{Ca}(\text{OH})_2$ per litre.*)

A saturated solution of calcium hydroxide is about 0.04 normal. It is made by shaking up excess of freshly slaked lime with water in a Winchester quart bottle, which is then set aside for some days until the solution has become clear. The clear solution is then siphoned into another empty Winchester similar to that used for baryta solution, the carbon dioxide in the burette and bottle having been previously removed by means of a current of purified air.

Calcium hydroxide solution is standardised in the same manner as baryta solution.

ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI.

Acetic Acid in Vinegar.

The acidity of a sample of pure vinegar is due almost entirely to acetic acid, and, even in adulterated vinegar, other acids are rarely found; the total acidity of the vinegar may therefore be attributed to acetic acid. The concentration of acetic acid in commercial vinegars varies widely but is usually between 4 and 5 per cent. The vinegar, whether coloured or not, is titrated with normal sodium hydroxide using phenolphthalein as indicator.

Dilute the measured quantity of vinegar (25 c.c.) with about twice as much water, to diminish the loss of acetic acid by volatilisation. Add 2 c.c. of phenolphthalein, and titrate the solution at once with normal sodium hydroxide. The first tinge of pink can be seen even with dark vinegars, but if there is any doubt about the end-point the colour of the solution should be compared with that of the same amount of vinegar diluted to the same extent with water: the colour change is then very readily detected.

Calculate the concentration of acetic acid in grams per litre. It is customary, however, to express the result as the percentage by weight of acetic acid. The density at 15° of 5 per cent. vinegar is about 1.019, and it may therefore be assumed, without serious error, that 1 litre of vinegar weighs 1020 grams. On this basis, calculate the percentage by weight of acetic acid.

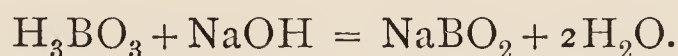
Borax.

Boric acid is a very weak acid without influence on methyl orange, and borax may, therefore, be titrated with standard hydrochloric acid using this indicator. Sulphuric acid should not be used, as it does not give a sharp end-point in this titration.

Exercise.—Dissolve a weighed quantity (about 4 grams) of borax in water and titrate the solution with N hydrochloric acid, using methyl orange as indicator. Calculate the percentage of $\text{Na}_2\text{B}_4\text{O}_7$ in the sample.

Borate in Borax.

If boric acid is titrated with sodium hydroxide, using phenolphthalein as indicator, the pink colour appears before all the boric acid is neutralised—on account of hydrolysis of the sodium borate. If glycerol or mannitol is added, the hydrolysis is prevented and the end-point of the titration then corresponds to complete neutralisation of the boric acid, according to the equation :



It is therefore possible to determine boric acid by titration with standard sodium hydroxide if glycerol (free from acid) or mannitol is added prior to the titration.

Procedure.—Weigh accurately about 3.5 grams of borax, transfer it to a 300 c.c. beaker, and dissolve it in about 180 c.c. of water. Add 2 c.c. of methyl orange, and then dilute hydrochloric acid until the solution is slightly acid. Then run in dilute (about decinormal) sodium hydroxide until the solution is neutral to methyl orange. (The solution now contains sodium chloride and boric acid.) Transfer the solution to a 250 c.c. standard flask, dilute to the graduation mark with water, and mix thoroughly.

Determine whether the glycerol that is to be used is neutral. If a 5 c.c. sample, to which phenolphthalein has been added, does not give a pink coloration with the first drop of a very dilute (about centinormal) sodium hydroxide solution, take a larger sample, add phenolphthalein, and then sodium hydroxide until a faint pink coloration is obtained.

To 25 c.c. of the prepared boric acid solution, add 15 c.c. of glycerol, and titrate with decinormal sodium hydroxide, using phenolphthalein as indicator. The end-point is reached when the yellowish solution shows a pink coloration. The pink colour should persist on the addition of a little more glycerol; should it disappear, continue the titration until the pink colour is no longer discharged by the addition of more glycerol. The sodium hydroxide must be free from carbonate. If mannitol is used instead of glycerol, 2 to 3 grams is sufficient.

Calculate the percentage of BO_3 in the sample of borax and also the corresponding percentage of anhydrous borax, $\text{Na}_2\text{B}_4\text{O}_7$.

Sulphuric Acid in the Concentrated Acid.

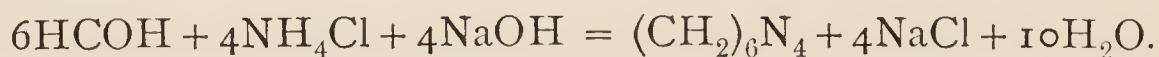
The concentration of sulphuric acid in the commercial product is usually expressed as the percentage by weight of H_2SO_4 , and it may be very roughly ascertained by finding the density of the acid and consulting the table given on p. 422. Since the density of sulphuric acid attains a maximum at about 97 per cent. and varies but little with the concentration above 94 per cent., a more accurate determination of the percentage of H_2SO_4 in a sample of the commercial acid may be made by titration, as follows:—

Weigh accurately in a tared weighing-bottle about 13 grams (about 7 c.c.) of the concentrated acid. (Since the acid is hygroscopic, avoid unduly exposing it to the air.) Two-thirds fill a 250 c.c. standard measuring-flask with water, and pour in through a funnel as much as possible of the acid. Wash in the remainder by means of a jet of water. Rinse the funnel and remove it. Mix the acid and water thoroughly by imparting a rotary movement to the liquid, and cool under the tap until the liquid is at the room temperature. Dilute to the graduation mark, and mix thoroughly.

Titrate portions of 25 c.c. with normal sodium hydroxide, using methyl red or methyl orange as indicator. From the results, calculate the percentage by weight of H_2SO_4 in the original concentrated acid.

Formaldehyde.

Formaldehyde interacts readily with ammonium salts in aqueous solution, forming hexamethylene-tetramine, and liberating the acid originally combined with the ammonia. The acid can be determined by titration, and from the data obtained the amount of formaldehyde in the sample may be calculated.



Procedure.—Dilute 5 c.c. of formaldehyde (commercial formalin) to 100 c.c. in a standard flask. Place 20 c.c. of this

solution in a conical flask, add 1 c.c. of litmus solution, and, if the formalin solution is acid, neutralise it by the careful addition of very dilute (about centinormal) sodium hydroxide. Then add about 1 gram of ammonium chloride and 25 c.c. of seminormal sodium hydroxide. Cork the flask and set it aside for at least half an hour. Titrate the solution with seminormal hydrochloric acid, using litmus as indicator.

Solubility of Lime in Water.

Prepare N/25 hydrochloric acid solution by diluting 10 c.c. of normal acid to 250 c.c. with water, using a standard pipette and flask. (The concentration of this solution will be one twenty-fifth of that of the original acid.)

Shake up some lime with water in a 500 c.c. stoppered bottle and set aside for two or three days until the solid has settled. From narrow glass tubing (4 mm. diameter) make a small siphon fitted with a piece of rubber tubing and a spring clip on the longer limb. Fill the siphon with water, and siphon about 100 c.c. of the clear "lime-water" (reject the first 20 c.c.) into a clean, dry flask. Cork the flask. Titrate 25 c.c. of the solution with N/25 acid, using phenolphthalein as indicator. From the result calculate the solubility of calcium hydroxide in grams per litre.

Hydroxide and Carbonate in Lime.

(1) Determine the total alkali (hydroxide plus carbonate) as follows:—Weigh accurately about 0.8 gram of the powdered lime, and transfer to a conical flask. Add 25 c.c. of normal hydrochloric acid, and warm gently until the lime has dissolved. (A small quantity of insoluble matter usually remains.) Cool the solution, and titrate the excess of acid with normal sodium hydroxide, using methyl orange as indicator. (The colour of the indicator often fades gradually during this titration, and more must be added at intervals.)

(2) Determine the hydroxide as follows:—Weigh accurately about 1.6 gram of the powdered lime, and transfer it to a dry, stoppered bottle (200 c.c.). Add 2 c.c. of alcohol and 100 c.c. of a 10 per cent. sugar solution—both measure-

ments being made accurately with pipettes. (The alcohol prevents the lime forming lumps when the sugar solution is added.) Shake the bottle more or less continuously for about half an hour. Filter through a dry paper and collect the filtrate (after rejecting the first 5 c.c.) in a dry beaker. Titrate 50 c.c. of the filtrate with normal hydrochloric acid, using methyl orange as indicator.

From the results obtained in (1) and (2), calculate the percentages of calcium hydroxide and calcium carbonate in the lime. In calculating the former, it may be assumed that the volume of the whole filtrate in (2) is 102 c.c.

Acidic Radical in Salts of Heavy Metals.

A solution of the salt is decomposed by means of hydrogen sulphide whereby an insoluble sulphide is precipitated and an equivalent amount of acid remains in solution; *e.g.*,



After separating the insoluble sulphide by filtration, the acid filtrate is titrated with standard alkali. This method is applicable to the determination of the acidic radical in many salts of the heavy metals. It is assumed that no free acid is present in the original solution except that derived from hydrolysis of the salt.

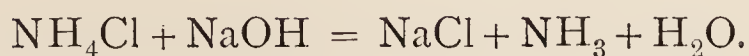
Exercise.—Dissolve about 0.25 gram (accurately weighed) of copper sulphate in hot water, add about 5 grams of pure sodium chloride, and precipitate the copper with hydrogen sulphide. Filter, and wash the precipitate with hydrogen sulphide solution (*cf.* pp. 28 and 174). Boil the mixed filtrate and washings until most of the hydrogen sulphide is expelled. Cool, and titrate with *decinormal* sodium hydroxide, using methyl orange as indicator.

Calculate the percentage of SO_4 in the salt.

Ammonia (*Indirect Method*).

(1) When an ammonium salt, such as ammonium chloride, is decomposed by boiling with an excess of sodium hydroxide solution, ammonia is liberated and an equivalent amount

of sodium hydroxide is used up, in accordance with the equation :



If a known quantity of sodium hydroxide (in excess of that required to decompose the ammonium salt) is used, and if, after the decomposition is complete, the residual sodium hydroxide is determined, the difference between these quantities gives the amount of sodium hydroxide equivalent to the ammonium salt taken.

If the ammonium salt contains free acid, the solution must be accurately neutralised before adding a measured excess of alkali; or the amount of acid present must be determined by a separate titration and allowed for in the calculation. The ammonium radical in salts like ferrous ammonium sulphate cannot be determined by this method.

Procedure.—Weigh accurately about 1 gram of the substance (*e.g.* ammonium sulphate), wash it into a 250 c.c. conical flask, and dilute the solution to about 25 c.c. Add a measured excess (25 c.c.) of normal sodium hydroxide solution, and boil gently to expel the ammonia. At intervals of about five minutes, test for ammonia in the escaping steam with a piece of moist red litmus paper—the test paper being held outside the flask. When the decomposition is complete, *i.e.* when no ammonia can be detected in the steam, cool the solution and titrate with standard hydrochloric acid, using methyl orange as indicator.

Calculate the percentage of NH_3 in the substance.

(2) Another method is a modification of that described on p. 68 for the determination of formaldehyde. The procedure is as follows:—Dissolve a weighed quantity of the ammonium salt (*e.g.* 0.4 to 0.5 gram of ammonium sulphate) in water and dilute the solution to 100 c.c. in a standard flask. Place 25 c.c. of the solution in a conical flask, add 5 c.c. of formalin (neutral to phenolphthalein) and 25 c.c. of decinormal sodium hydroxide. Cork the flask and set it aside for about fifteen minutes. Titrate the excess of alkali with decinormal hydrochloric acid, using phenolphthalein as indicator.

Ammonia (*Direct Method*).

OUTLINE OF METHOD.—The substance is boiled with excess of sodium hydroxide solution, and the ammonia evolved is absorbed by a known volume of a standard acid solution. The amount of acid neutralised by the ammonia is then determined by titration of the excess of acid with standard alkali.

Procedure.—Arrange the apparatus as shown in Fig. 30. A is a copper flask of about 2 litres capacity. (A glass

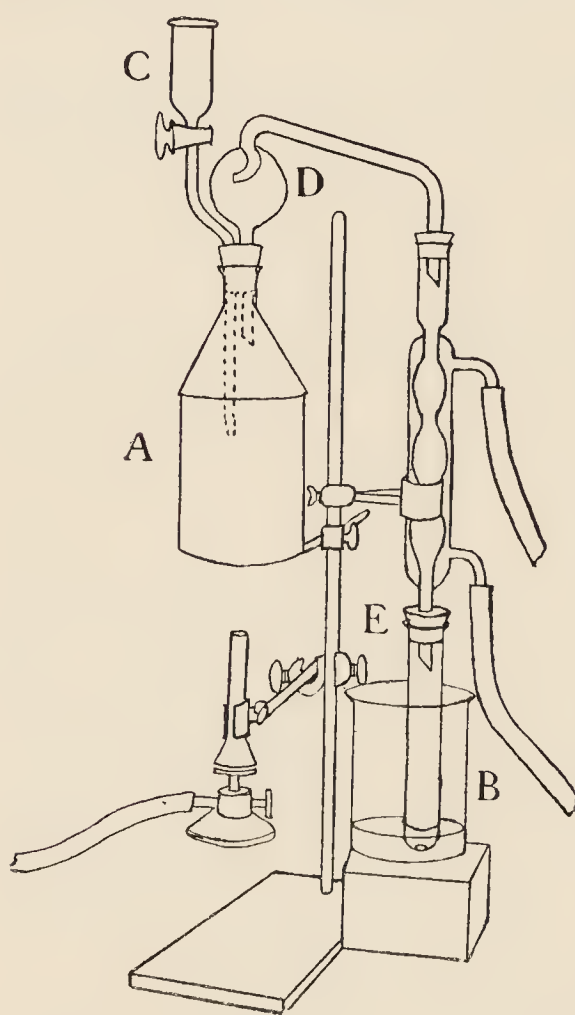


FIG. 30.

flask may be used, but glass vessels often break when used with a boiling alkaline solution.) Fit the flask with a two-holed rubber cork to carry the tap-funnel C and the tube leading to the condenser. It is advisable to have a trap at D to prevent any drops of sodium hydroxide being driven over during the boiling.¹ Wet the inner tube of the condenser with water, and attach a boiling-tube with a hole in the bottom. B is a 600-700 c.c. beaker. A convenient arrangement is to place B on a wood block, so that the beaker can be lowered or removed by taking away the block.

Examine the apparatus carefully to be sure that there is no leakage at any of the corks. Introduce into the tap-funnel a known quantity² of the substance to be analysed, and wash it into the flask with water. In the beaker B place a measured volume (25 or 50 c.c.) of standard acid, and add to it an equal volume of water and 2 c.c. of methyl red.

When these preparations are completed, run into the

¹ The trap is more efficient if a hole is made in the *side* of the tube leading from the copper flask into D; the hole must be situated below the rubber stopper.

² In general, the amount of substance to be taken for analysis must be regulated by the results of qualitative analysis.

large flask through the tap-funnel an excess of sodium hydroxide solution, and close the tap as soon as all the alkali has entered. As a rule about 50 c.c. of 2N sodium hydroxide will be sufficient. Add sufficient distilled water (400 c.c.) to ensure that the contents of A will not be evaporated to dryness during the experiment.

It is of course essential that all the ammonia evolved should be caught by the standard acid in the absorption flask. The only risk of loss is while the air in the large flask is being expelled. Apply heat therefore, cautiously, so that there is no sudden rush of gas through the standard acid. Boil for thirty minutes. In that time all the ammonia should be over, but it is well to make sure. Disconnect at E, and test the distillate with litmus paper. If it is still alkaline, the boiling must be continued.

When all the ammonia has been driven over, *open the tap C before extinguishing the flame*, disconnect the apparatus, and titrate the solution in B to find how much of the acid remains unneutralised.

In order to avoid over-stepping the end-point when titrating the large volume of liquid, proceed as follows:—Transfer about one-third of the liquid in B to a smaller beaker. Run standard alkali into the main portion in B until the neutral point is slightly over-stepped. Add about one-half of the portion in the small beaker, then more standard alkali as before, followed by more of the reserve portion, and so on until all the reserve portion has been added, when the end-point can be accurately adjusted. Finally, pour some of the neutral liquid into the small beaker, pour it back into B, and add a further half-drop of alkali if required.

Another Absorption Apparatus.—The apparatus described above for the absorption of the ammonia has the advantage of simplicity, and there is little risk of losing ammonia if the heating is carefully regulated. With the form of absorption apparatus shown in Fig. 31, there is much less risk of losing ammonia. The flask is fitted with a two-holed rubber cork carrying an adapter G for the end of the condenser and a tube H filled with glass beads. At the start of an experiment with this form of apparatus, the measured



FIG. 31.

volume of standard acid is run in through the tube H so as to moisten the beads with acid. One or two drops of methyl red are then poured on the beads; the red coloration produced must persist to the end of the distillation.

When all the ammonia has been driven over, the liquid in H is washed down into the flask prior to the titration.

Exercise.—Determine the percentage of NH_3 in ammonium sulphate. Use from 1.3 to 1.5 gram (accurately weighed) and absorb the ammonia with 25 c.c. of normal acid.

Nitrate.

The nitrate is reduced to an ammonium salt by means of (a) iron and sulphuric acid, or (b) titanous chloride and sodium hydroxide. The ammonia is then determined in the usual manner.

Procedure.—(a) Place a weighed portion of the substance in a 500 c.c. conical flask, and add 10 grams of reduced iron (B. P. ferrum redactum) and 50 c.c. of water. Fit the flask with a rubber cork and reflux condenser. (A reflux condenser is a condenser placed upright above the flask so that the condensed liquid runs back into the flask.) Add 20 c.c. of a mixture of two parts of water and one part of concentrated sulphuric acid, and boil gently for five minutes. Remove the flame, and rinse back into the flask any liquid that has collected on the inner surface of the condenser. Boil again for five minutes and cool. Transfer the contents of the conical flask to the copper flask (Fig. 30), and determine the ammonia by the direct method. Take care to add *sufficient sodium hydroxide* (about 15 grams) before distilling.

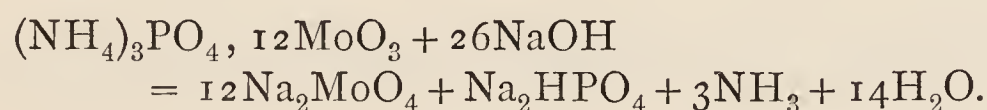
(b) Place a weighed quantity of the nitrate in the copper flask and add about 100 c.c. of 2N sodium hydroxide solution. While swirling the contents of the flask, add 20 c.c. of commercial titanous chloride (15 per cent. solution). Without delay, connect the flask with the condenser, add about 150 c.c. of water through the tap-funnel, and distil off the ammonia into a measured volume of standard acid.

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre). For method (a) use about 1.5 gram and collect the ammonia in 25 c.c. of normal acid. For method (b) dissolve about 1.5 gram in

water and dilute the solution to 250 c.c. in a standard flask. Use 25 c.c. of this solution and collect the ammonia in 25 c.c. of decinormal acid.

Phosphate.

The phosphate is precipitated as ammonium phosphomolybdate and the precipitate is filtered and washed. The precipitate is then decomposed by boiling with a measured volume of standard sodium hydroxide solution, and the excess of alkali is titrated with standard acid.



From the above equation it may be seen that 1 gram-atom of phosphorus requires 26 gram-molecules of sodium hydroxide, and therefore 1 c.c. of normal alkali is equivalent to 0.00119 gram P, or 0.00273 gram P_2O_5 .

Procedure.—Take a measured volume of the phosphate solution (containing not more than 10 milligrams of P_2O_5) in a 400 c.c. beaker, add 10 grams of ammonium nitrate and 3 c.c. of concentrated nitric acid, and heat to about 65° . Heat 20 c.c. of 3 per cent. ammonium molybdate solution to 65° and add it slowly from a dropping-tube (p. 171), with constant stirring, to the phosphate solution. Set the beaker aside for about half an hour.

Filter through paper-pulp on a 1-cm. porcelain disc (see p. 30). Transfer the precipitate to the filter and wash the beaker and the precipitate with 0.1 per cent. potassium nitrate solution until the filtrate is free from acid. (This will require at least 100 c.c. of washing solution; test the later washings with a few drops of methyl orange.) Transfer the precipitate together with the paper-pulp and porcelain disc to the original beaker, and add from a burette rather more than sufficient decinormal sodium hydroxide (free from carbonate) to dissolve the precipitate completely. Run some of the sodium hydroxide solution through the funnel to remove any adhering precipitate and rinse the funnel into the beaker.

Dilute the solution to about 150 c.c. and boil gently for twenty minutes to expel ammonia. Without cooling, add phenolphthalein and run in (from a burette) decinormal

sulphuric acid in slight excess. Boil again for five minutes to expel carbon dioxide. Cool under the tap and finally titrate the excess of acid with decinormal alkali. The first definite pink colour marks the end-point, but the colour fades somewhat rapidly.

Exercise.—Determine the percentage of P_2O_5 in potassium dihydrogen phosphate (A.R.), KH_2PO_4 . Weigh accurately from 0.17 to 0.19 gram of the salt (after drying it at 120° for an hour), dissolve in water, and dilute the solution to 250 c.c. in a standard flask. Use 25 c.c. of the solution for each determination.

Determination of Phosphorus in Steel.—Place a weighed quantity (1.5 to 1.6 gram) of the steel in a covered 300 c.c. beaker, add 30 c.c. of water and 10 c.c. of concentrated nitric acid, and warm on a hot-plate until the steel has dissolved. Add 3 c.c. of potassium permanganate solution (0.5 per cent.) and boil for three minutes to destroy carbides and complete the oxidation of the phosphorus. Then add enough ferrous sulphate (about 3 c.c. of a 3 per cent. solution containing sulphuric acid) to dissolve the precipitated manganese dioxide. Boil the solution to expel oxides of nitrogen. Rinse the cover glass and add 8 grams of ammonium nitrate and 10 c.c. of concentrated nitric acid. Precipitate the phosphate at about 65° by adding 50 c.c. of ammonium molybdate solution, and complete the determination by the alkalimetric method described above.

From the data obtained, calculate the percentage of phosphorus in the sample of steel.

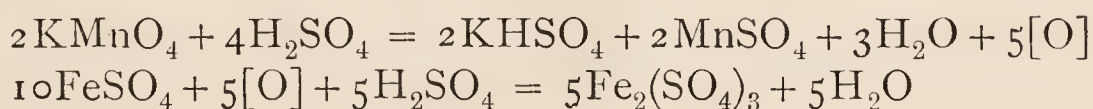
Standard Potassium Permanganate and Dichromate

DECINORMAL POTASSIUM PERMANGANATE.

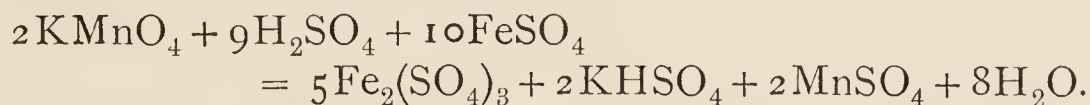
(*N/10 solution contains 3.161 grams $KMnO_4$ per litre.*)

NEARLY all of the determinations commonly made with potassium permanganate are carried out in an acid solution. Hydrochloric acid is avoided, if possible, because it may be oxidised by the permanganate (see p. 92), and since nitric acid, like the permanganate, is an oxidising agent, its presence is not desirable. Sulphuric acid is the most suitable acid, and it is almost always added in titrations that are to be carried out with permanganate in an acid solution.

Potassium permanganate in presence of sulphuric acid oxidises ferrous sulphate as follows:—



or, combining these equations,



The first equation shows that two molecules of the permanganate provide five atoms of available oxygen. A solution that contains one-fifth of the molar weight per litre will provide 8 grams of oxygen per litre and is described, therefore, as a normal solution. A decinormal solution contains one-fiftieth of the molar weight per litre, *i.e.*, 3.161 grams.

Standard solutions of potassium permanganate should be prepared from a well-crystallised specimen of the salt, in the form of brilliant black crystals with a metallic lustre,

free from any blue or violet iridescence. A solution prepared from the pure salt and water free from organic matter is very stable, but the salt of commerce (including some brands described as "for analysis") usually contains a small quantity of manganese dioxide, and this impurity brings about progressive decomposition of the solution, slowly at first and afterwards more rapidly. If the suspended oxide is completely removed by careful filtration, the solution will remain unchanged for many months if protected from bright sunlight.

Weigh about 3.2 grams of potassium permanganate. Transfer the crystals (which must not be powdered) to a clean flask and add about 500 c.c. of cold distilled water. Shake the flask at intervals and set it aside overnight. Filter the solution—through a funnel containing a plug of glass wool covered with a little asbestos—into a clean, graduated litre flask and dilute the filtered solution to the mark. Transfer the solution to a thoroughly clean, glass stoppered bottle. (The bottle should be cleaned with chromic acid solution and afterwards rinsed with distilled water.)

On account of the action of potassium permanganate solution on rubber, the burette used for the solution must have a glass tap. Since the meniscus cannot be clearly seen through the deep purple solution (unless it is very dilute), the burette readings are taken at the highest level of the liquid surface which, against a white card, appears as a sharp, horizontal line. A burette that has been used for permanganate solution should be emptied and cleaned immediately after use. Brown stains of manganese oxides can be removed with sulphurous acid.

As already explained, most permanganate titrations are carried out in presence of sulphuric acid, and sufficient acid must be added—*before beginning the titration*—to prevent the formation of a permanent brown coloration or a brown precipitate. The permanganate solution must be run in slowly, with continuous stirring or very frequent shaking. No indicator other than the permanganate itself is required, and the end-point of the titration is easily recognised. A single drop of decinormal permanganate solution is sufficient to impart a distinct pink colour to 200 c.c. of water. An endeavour should be made to keep the volume of the solution

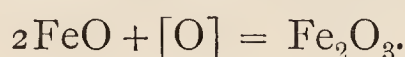
at the end-point of all titrations as nearly constant as possible—in general, about 100 c.c.—in order that a constant excess of permanganate will be required to give the same intensity of pink colour. Greater accuracy will thereby result.

Permanganate solutions may be standardised with ferrous ammonium sulphate, sodium oxalate, oxalic acid, or potassium tetroxalate, all of which are obtainable as “analytical reagents” of a definite standard of purity. Sodium oxalate is probably the best standard for the purpose.

Standardisation with Ferrous Ammonium Sulphate.—

The formula of ferrous ammonium sulphate is $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Weigh accurately from 1.0 to 1.1 gram, wash into a conical flask containing about 25 c.c. of dilute sulphuric acid, dilute the solution to about 70 c.c., and run in the permanganate solution slowly, with frequent shaking, until a faint permanent pink coloration is obtained.

Calculation.—The oxidation of a ferrous to a ferric compound may be represented in its simplest form by the equation



It is evident that 55.84 grams of iron are oxidised by 8 grams (1 gram-equivalent) of oxygen. But the molar weight (392.1 grams) of ferrous ammonium sulphate contains 55.84 grams of iron, and is oxidised therefore by 8 grams of oxygen, *i.e.* by 1 litre of normal permanganate.

If 26.80 c.c. of the permanganate oxidises 1.052 gram of ferrous ammonium sulphate,

$$1 \text{ litre will oxidise } \frac{1.052 \times 1000}{26.80} \text{ grams.}$$

But 1 litre of normal permanganate will oxidise 392.1 grams. Therefore the permanganate solution is

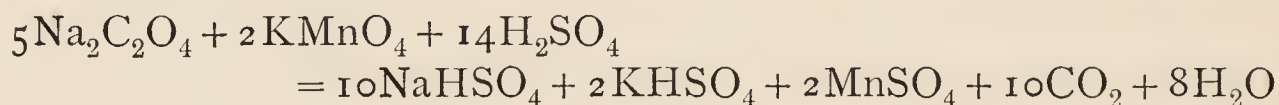
$$\frac{1.052 \times 1000}{26.80 \times 392.1} = 0.1001 \text{ N.}$$

Standardisation with Sodium Oxalate.—Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, is an anhydrous salt, and it may be dried before use by heating in an air-oven for an hour at 120° .

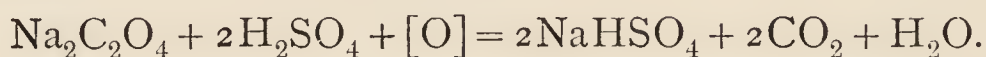
Weigh accurately from 0.17 to 0.19 gram of the salt. Wash it into a conical flask, add 25 c.c. of dilute sulphuric acid, and dilute to about 70 c.c. Heat the solution to about

90° (just short of boiling). Titrate the hot solution by running in the permanganate *very slowly*, while shaking the flask continuously. When near the end-point heat the solution again if the temperature has fallen below 60°, and allow each drop (or half-drop) of permanganate to become completely decolorised before adding the next. A very faint, permanent pink coloration marks the end-point. (The formation of a brown precipitate or a permanent brown coloration during the titration indicates that the solution is too cold and that the permanganate has been added too quickly, or that insufficient sulphuric acid is present.) Repeat the titration with another weighed portion of the sodium oxalate.

The oxidation of sodium oxalate by potassium permanganate in presence of sulphuric acid may be represented by the equation—



or in simpler form by the equation



It may be seen from the second equation that 1 mole of sodium oxalate (134.0 grams) requires 16 grams of oxygen. Therefore 67.0 grams of sodium oxalate require 8 grams of oxygen, or 1 litre of normal permanganate solution.

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$, or potassium tetroxalate, $\text{KHC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$, may be used instead of sodium oxalate for the standardisation. One litre of normal permanganate solution will oxidise 63.03 grams of oxalic acid and 63.55 grams of the tetroxalate, and from 0.16 to 0.18 gram of either substance is required for a single titration.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE.

One of the most important determinations that can be made by means of a standard solution of potassium permanganate is that of iron. Iron can be determined, however, equally well with standard potassium dichromate, and all the examples of analysis involving the determination of iron are

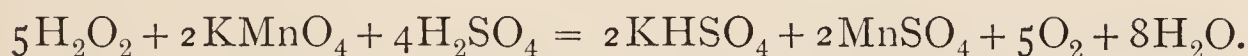
given after the preparation and use of a standard dichromate solution have been described (see p. 92).

Oxalic Acid and Oxalates.

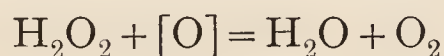
The procedure is described under the standardisation of permanganate with sodium oxalate.

Peroxides and Dioxides.

Hydrogen Peroxide.—In presence of sulphuric acid, hydrogen peroxide and potassium permanganate solutions interact as follows :—



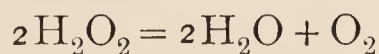
The decomposition of the hydrogen peroxide may be represented more simply by the equation



which shows that 17.01 grams of hydrogen peroxide require 8 grams of oxygen, or 1 litre of normal permanganate.

The concentration of commercial hydrogen peroxide may be determined as follows :—Dilute 10 c.c. of the solution to 250 c.c. in a standard flask. After mixing, measure 25 c.c. into a conical flask, and dilute to about 300 c.c. Add 25 c.c. of dilute sulphuric acid, and titrate with decinormal permanganate.

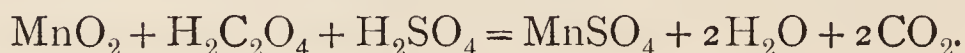
The commercial practice is to express the concentration of hydrogen peroxide solutions in terms of the volume of oxygen obtainable from them on decomposition by heat. Thus “ten volumes” hydrogen peroxide refers to a solution of which 1 c.c. will yield 10 c.c. of oxygen. It should be observed that the decomposition of hydrogen peroxide by heat,



liberates only half the quantity of oxygen obtainable from it by oxidation with permanganate.

From the result obtained in the titration, calculate the concentration of the original solution (1) as the percentage by weight of H_2O_2 , taking the specific gravity as unity, (2) in terms of the oxygen value, assuming the oxygen to be measured at N.T.P.

Valuation of Manganese Dioxide (Pyrolusite).—The dioxide is boiled with excess of oxalic acid and dilute sulphuric acid until the reaction is complete. Part of the oxalic acid is oxidised by the dioxide and the residual portion is determined by titration with standard permanganate. The equation is



Prepare an approximately 0.2 normal solution of oxalic acid by dissolving about 3 grams of the crystals in 250 c.c. of water. Dilute 10 c.c. of this solution to 50 c.c., add 25 c.c. of dilute sulphuric acid, and titrate (at 70° to 80°) with standard permanganate.

Weigh accurately about 0.4 gram¹ of *finely powdered*² pyrolusite in a small weighing tube (small test-tube). Transfer the pyrolusite to a conical flask (about 250 c.c.) and reweigh the tube. Measure 50 c.c. of the oxalic acid into the flask, add 25 c.c. of dilute sulphuric acid, place a small funnel in the mouth of the flask, and boil gently until no black particles remain undissolved. (A small residue of silica is usually present.) Add water to replace that lost by evaporation, and titrate (at 70° to 80°) with standard permanganate.

Calculation.—0.4084 gram of pyrolusite was boiled with 50 c.c. of an oxalic acid solution. The residual oxalic acid required 24.60 c.c. of 0.1025N permanganate. Also, 10 c.c. of the oxalic acid solution required 21.20 c.c. of the permanganate, and therefore 50 c.c. requires 106.0 c.c. Therefore the MnO_2 is equivalent to $106.0 - 24.60 = 81.40$ c.c. of 0.1025N permanganate.

From the equation it may be seen that MnO_2 is reduced to manganous sulphate, corresponding to MnO , and 43.46 grams MnO_2 yield 8 grams of oxygen. One c.c. of normal permanganate therefore corresponds to 0.04346 gram MnO_2 . The percentage of MnO_2 in the sample is therefore

$$\frac{81.4 \times 0.1025 \times 0.04346 \times 100}{0.4084} = 88.9.$$

¹ If it is probable that the sample contains less than 75 per cent. of manganese dioxide, a larger quantity should be taken.

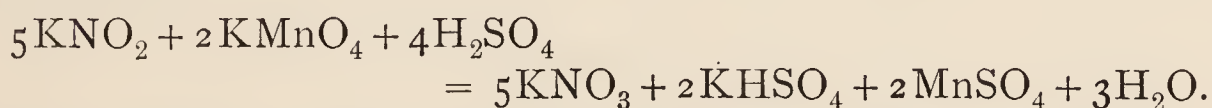
² It is imperative that the sample be very finely powdered.

In place of oxalic acid, ferrous sulphate may be used. In that case, the flask must be provided with a Bunsen valve or with a delivery tube dipping into sodium carbonate solution, in order to protect the ferrous sulphate from atmospheric oxidation (see p. 93).

Lead Dioxide and Red Lead.—A weighed quantity (1 gram of PbO_2 or 2.5 grams of Pb_3O_4) is boiled with 25 c.c. of dilute nitric acid and 50 c.c. of 0.2 normal oxalic acid until completely dissolved, and the analysis is finished in the same manner as described for pyrolusite.

Nitrite.

The oxidation of a nitrite to a nitrate by potassium permanganate in presence of sulphuric acid is shown by the equation



The oxidation is essentially represented by the equation



The molar weight (85.1 grams) of potassium nitrite requires 16 grams of oxygen, and therefore 42.6 grams requires 1 litre of normal permanganate. The oxidation must be carried out in such a manner as to avoid the loss of nitrous acid that would occur if the nitrite solution were made acid before the permanganate is added.

Procedure.—Prepare a standard (approximately decinormal) solution of oxalic acid by dissolving about 1.5 gram of the crystals in 250 c.c. of water and titrating 25 c.c. of the solution with decinormal permanganate in the usual way.

Make a preliminary titration of the nitrite solution to find how much standard permanganate (approximately) is required to oxidise a measured volume of it:—Dilute 10 c.c. of the nitrite solution to about 100 c.c. in a conical flask and warm to about 70° . Add 5 c.c. of dilute sulphuric acid and run in standard permanganate until a permanent, decidedly pink, coloration is obtained. Note the volume required. An accurate determination is then made as follows:—

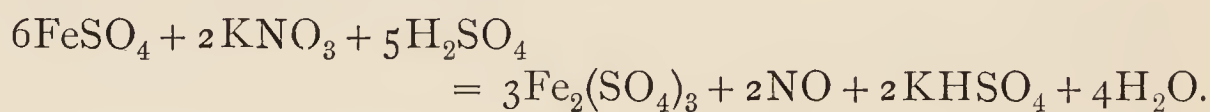
Measure into a conical flask not less than three times

the volume of standard permanganate required in the preliminary titration, *i.e.* more than sufficient to oxidise 25 c.c. of the nitrite solution. Add 25 c.c. of dilute sulphuric acid, dilute to 200 c.c., and warm the solution to about 50°. Run 25 c.c. of the nitrite solution slowly into the excess of permanganate, with continuous shaking, and then add 10 c.c. of concentrated sulphuric acid and heat the mixture to about 80° to complete the oxidation. To the hot solution add (from a burette) a measured excess of standard oxalic acid (sufficient to decolorise the solution), and titrate the excess of oxalic acid with standard permanganate.

Exercise.—Determine the percentage of potassium nitrite in a sample of the commercial salt. Weigh accurately from 1 to 1.2 gram of the nitrite, dissolve in cold water and dilute to 250 c.c. in a standard flask. Use 25 c.c. for each titration.

Nitrate.

When a solution of ferrous sulphate is boiled with a nitrate and excess of sulphuric acid, the ferrous sulphate is oxidised and nitric oxide is set free.



If, therefore, a known quantity of ferrous sulphate is taken, the amount of nitrate present can be calculated from the amount of ferrous sulphate that becomes oxidised in the process. Air must be carefully excluded during the process, more especially as nitric oxide and oxygen form nitrogen peroxide which would then oxidise more of the ferrous sulphate. The air is accordingly displaced by a current of carbon dioxide. The mixture must contain from 35 to 40 per cent., by volume, of concentrated sulphuric acid.

The apparatus is shown in Fig. 32. It consists of a 400 c.c. conical flask, fitted with a reflux condenser, and provided with a tube A, through which the carbon dioxide enters. A U-tube, containing a little water, is attached to the top of the condenser. The carbon dioxide is supplied from a Kipp generator. If the generator has been freshly charged, the air must be carefully displaced before using the gas.

Procedure.—Prepare a solution of ferrous sulphate by dissolving about 7 grams of the crystals in cold water mixed with 10 c.c. of dilute sulphuric acid and dilute the solution to 250 c.c. Titrate 25 c.c. of the solution with decinormal permanganate.

Weigh accurately 1.2 to 1.3 gram of the nitrate, dissolve in water, and dilute the solution to 500 c.c. in a standard flask. Measure 25 c.c. of the solution into the conical flask, and add 25 c.c. of the ferrous sulphate solution. Connect the flask with the condenser, and pass a rapid current of carbon dioxide through the apparatus for five minutes. Then, without interrupting the current of carbon dioxide, immerse the flask in cold water, remove the U-tube, and slowly introduce, through the condenser, 30 c.c. of concentrated sulphuric acid. Replace the U-tube, and reduce the amount of carbon dioxide entering the flask until about one bubble of gas per second passes through the water in the U-tube. Boil the contents of the flask for ten minutes. Increase the rate of the carbon dioxide again, and cool the solution by immersing the flask in water. Detach the flask and rinse the carbon dioxide inlet-tube into it. Dilute the solution to about 150 c.c., and titrate the residual ferrous sulphate with decinormal permanganate.

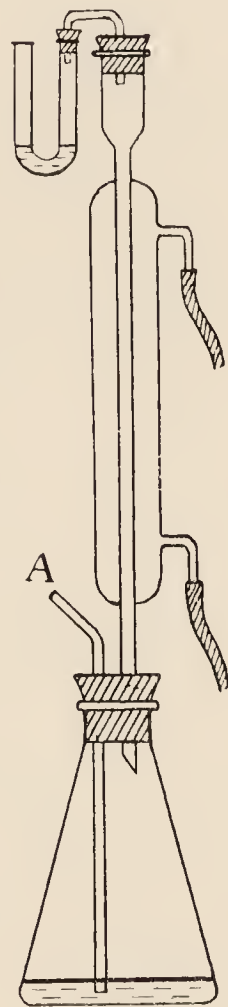


FIG. 32.

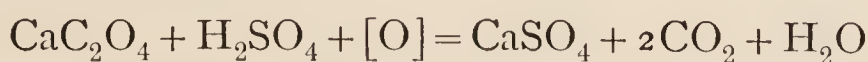
One c.c. of normal permanganate corresponds to 0.02834 gram NaNO_3 .

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre).

Calcium.

The calcium is precipitated as calcium oxalate. The washed precipitate is dissolved in sulphuric acid and the solution is titrated with standard permanganate.

From the equation



it may be seen that the molar weight of CaC_2O_4 (containing

40.07 grams Ca) requires 2 gram-equivalents of oxygen. Therefore 1 c.c. of normal permanganate corresponds to 0.02004 gram Ca.

Exercise.—Weigh accurately about 0.15 gram of powdered calcspar. Transfer to a 300 c.c. beaker, add 10 c.c. of water and 5 c.c. of dilute hydrochloric acid, and cover the beaker with a clock-glass. Warm until the calcspar has dissolved, then dilute with a little water and boil the solution for a few minutes in order to free it from carbon dioxide. Rinse the clock-glass into the beaker and add a few drops of methyl orange and then ammonia until the solution is neutral. Add 1 c.c. of dilute hydrochloric acid, dilute the solution to about 150 c.c., heat until boiling, and precipitate the calcium by slowly adding a boiling solution of ammonium oxalate. (Use a freshly prepared solution, about 2 per cent.) Now make alkaline with ammonia and boil for a few minutes, stirring in order to avoid “bumping.” Allow the precipitate to settle, and then make sure that precipitation is complete by adding a few more drops of the reagent. Place the beaker on the steam-bath for one hour.

Decant the supernatant liquid through a 9-cm. paper, wash the precipitate once by decantation, and then transfer it to the filter (see page 28). Wash the precipitate and filter paper with water containing a little ammonia, until the washings give no opalescence with nitric acid and silver nitrate. (Always rinse the end of the funnel stem before collecting a portion of the washings—about 5 c.c.—for a test like this.)

Now place under the funnel the beaker in which the precipitation was made, pierce the apex of the filter paper with a *pointed* glass rod, and wash the precipitate into the beaker with hot water. Pour about 25 c.c. of hot dilute sulphuric acid into the filter, taking care that the acid comes into contact with every part of the paper and that some of it is poured behind the double fold of the paper, in case any of the calcium oxalate has lodged there. Then wash the paper thoroughly with hot water. Heat the calcium oxalate solution to about 90°, and titrate with standard permanganate.

Calculate the percentage of calcium in the calcspar.

Manganese.

The following method is based on the fact that a manganous salt is oxidised to permanganic acid by sodium bismuthate in presence of acid. The permanganic acid is determined by adding a known excess of ferrous sulphate and titrating the excess with standard permanganate.

Commercial sodium bismuthate is a brown powder of somewhat indefinite composition; it may be regarded as NaBiO_3 —a salt of metabismuthic acid, HBiO_3 .

Very small quantities of manganese can be accurately determined by this method which is particularly well adapted for the determination of manganese in steels, ores, rocks, etc. The solution containing the manganese must be free from chloride; and the oxidation must be carried out in presence of either nitric acid or sulphuric acid.

The following solutions are required:—

Standard Potassium Permanganate Solution.—Dissolve 1 gram of the pure salt in cold water and dilute the solution to 1 litre. One c.c. corresponds to 0.0003475 gram Mn. (If the permanganate is of doubtful purity, the solution must be standardised.)

Nitric Acid Solutions.—(A) Dilute 250 c.c. of concentrated nitric acid to 1 litre. (B) Dilute 30 c.c. of concentrated nitric acid to 1 litre. (The concentrated nitric acid should be colourless, *i.e.* free from oxides of nitrogen.)

Sulphuric Acid Solution (3 per cent.).—Pour 20 c.c. of the concentrated acid into water and dilute the solution to 1 litre.

Ferrous Sulphate Solution.—Dissolve 9 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 400 c.c. of dilute sulphuric acid and dilute the solution to 1 litre. The value of this solution in terms of the standard potassium permanganate solution must be ascertained by carrying out a “blank” determination from day to day as follows:—Shake together in a flask 50 c.c. of nitric acid (A) with about 0.5 gram of sodium bismuthate, add 50 c.c. of nitric acid (B), and filter through a paper-pulp filter (p. 30).¹ Wash with 50 c.c. of nitric acid (B). To the

¹ The paper-pulp filter should be washed with a dilute solution of potassium permanganate containing sulphuric acid and then with water. The same pulp may be used for several successive filtrations.

filtrate add 25 c.c. of ferrous sulphate solution, and titrate at once with the standard permanganate.

Determination of Manganese in Steel.—Weigh accurately about 1 gram of the steel and transfer it to a 200 c.c. conical flask. Add 50 c.c. of nitric acid (*A*) and boil gently until the steel is dissolved and the solution free from oxides of nitrogen. Cool, add about 0.5 gram of sodium bismuthate (in order to oxidise combined carbon), and heat until the pink colour disappears. If manganese dioxide is precipitated, add sufficient sulphurous acid to clear the solution, and then boil for two to three minutes. Cool thoroughly under the tap, or in ice. Add about 2 grams of bismuthate and shake for two minutes. Dilute with 50 c.c. of nitric acid (*B*), filter through paper-pulp, and wash with dilute nitric acid (*B*). Add to the filtrate a measured excess of ferrous sulphate solution (10 c.c. to 50 c.c. according to the amount of manganese present), and titrate *at once* with the standard permanganate.

The percentage of manganese in the sample can then be readily calculated.

Determination of Manganese in Iron Ore.—Take from 0.5 to 2 grams of the ore. Dissolve the weighed portion by warming it in a 200 c.c. conical flask (Pyrex glass) with the minimum quantity of concentrated hydrochloric acid—with the addition of a little concentrated nitric acid if organic matter is present. Cool, and add (cautiously) 10 c.c. of concentrated sulphuric acid. Manipulate the flask, held in a hand-clamp, over a free flame until all hydrochloric acid is expelled and copious fumes of sulphuric acid are evolved. Add more sulphuric acid, if necessary, to provide about 8 c.c. in all. Allow to cool, dilute with 100 c.c. of water, and warm to dissolve the sulphates. Cool to about 40°, add 1 gram of bismuthate, and shake for at least two minutes. Filter through paper-pulp; rinse the flask and wash the filter with at least 100 c.c. of 3 per cent. sulphuric acid. Add to the filtrate (from a weighing-bottle) rather more ferrous ammonium sulphate than is sufficient to decolorise the permanganic acid. (Reweigh the bottle and contents to find the amount added.) Titrate the excess of ferrous salt with the permanganate.

From the data obtained calculate the percentage of manganese in the ore.

Antimony.

Potassium permanganate oxidises antimonious chloride in presence of hydrochloric acid to antimonic chloride, and antimony in alloys, such as solder, pewter, and type metal, may be determined volumetrically in this way. Lead and tin do not interfere, but if arsenic is present it must be removed or a correction made.

Determination of Antimony in Type Metal.—Weigh accurately about 0.5 gram of the alloy (in fine powder or thin foil). Place it in a 150 c.c. conical flask (Pyrex glass is best), and add 10 c.c. of concentrated sulphuric acid. Heat the mixture, gently at first, and then at the boiling-point of the acid until the alloy is completely disintegrated. It is best to manipulate the flask, held in flask tongs or a hand-clamp, over a free flame. Heating is continued until any undissolved lead sulphate is white or nearly so and all separated sulphur oxidised.

Allow the flask to cool. Add (cautiously) 25 c.c. of water and boil again for a few minutes to expel any sulphur dioxide. After cooling again, add 10 c.c. of concentrated hydrochloric acid and wash the contents of the flask into a larger flask. (Lead sulphate may remain undissolved.) Dilute to about 150 c.c., cool very thoroughly under the tap or in ice-water, and titrate with decinormal (or 0.05N) permanganate. A sharp end-point should be obtained but the pink colour fades somewhat rapidly.

DECINORMAL POTASSIUM DICHROMATE.

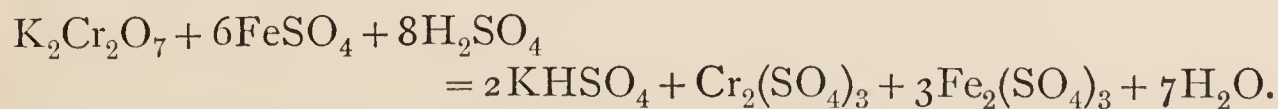
(N/10 solution contains 4.903 grams $K_2Cr_2O_7$ per litre.)

Weigh accurately about 4.9 grams of pure potassium dichromate. Transfer to a standard litre flask, dissolve in water, and dilute the solution to 1 litre.

The interaction between potassium dichromate and ferrous sulphate in presence of acid is as follows :—



or, combining these equations,



The molar weight of the dichromate thus provides 48 grams

(six gram-equivalents) of available oxygen, and a decinormal solution therefore contains one-sixtieth of the molar weight per litre. If the solution is prepared from pure potassium dichromate, the concentration should correspond exactly to the weight of the salt taken. Standard potassium dichromate is used only for the determination of iron, and 1 litre of a decinormal solution will oxidise 5.584 grams.

Dichromate, unlike permanganate, is unaffected by moderate quantities of hydrochloric acid, and it is therefore suitable for the titration of iron when stannous chloride has been used as reducing agent. It has no action on rubber and may be measured in a burette closed with rubber tubing and a pinchcock, instead of a glass tap. The solution is quite stable.

Method of Titration with Dichromate.—The solution to be titrated should be placed in a beaker (a flask is not convenient) and must contain considerable sulphuric or hydrochloric acid; add, therefore, about 25 c.c. of dilute acid, unless the solution is known to contain a corresponding quantity, and then run in the dichromate solution from a burette until all the iron is oxidised.

The green chromic salt formed during the titration obscures the colour change at the end-point, and few are able to detect it by eyesight. It is therefore usual to determine the end-point by means of potassium ferricyanide, which is used as an "external" indicator. *The ferricyanide solution must be freshly prepared and very dilute (about 0.1 per cent.), and must contain no ferrocyanide.* To prepare it, take a crystal of potassium ferricyanide weighing slightly more than 0.5 gram, rinse it several times with small quantities of cold water (in order to remove superficial ferrocyanide), and dissolve in 50 c.c. of water. Dilute 5 c.c. of this solution to 50 c.c. The solution decomposes somewhat rapidly, and a fresh one must be made from the solid for each set of titrations.¹

The titration is then carried out as follows:—Run in the dichromate solution slowly from a burette while stirring the ferrous solution, and from time to time place a drop of the latter on a *dry*, white tile and touch it with a drop of the

¹ After a little experience it is easy to prepare a solution of a suitable concentration by carefully rinsing a minute crystal of ferricyanide and dissolving it in a test-tube of water.

ferricyanide indicator ; the two drops should be placed side by side so that only marginal contact results. (A separate glass rod must be used for the ferricyanide, and after each test it should be placed in a beaker of water in order to rinse it.) If the solution still contains considerable ferrous salt, a blue coloration is obtained ; as the amount of ferrous salt diminishes, the blue coloration becomes less pronounced until only a faint blue tint is seen, and finally, when no trace of this can be detected after waiting for thirty seconds, no ferrous salt remains and the titration is finished.

If many drops are removed at an early stage of the titration, the accuracy is impaired, and a second titration must then be made in which almost the whole amount of the dichromate is added before any drops are removed for testing. The error due to the removal of drops is then negligible. If the ferricyanide contains ferrocyanide, it is impossible to obtain a sharp end-point, since ferric salts give a blue coloration with ferrocyanide. The ferricyanide drops must not be exposed to bright sunlight.

Standardisation.—The potassium dichromate solution must be standardised against ferrous ammonium sulphate or iron of known purity.

(1) Weigh accurately about 1 gram of ferrous ammonium sulphate, wash into a beaker containing about 25 c.c. of dilute sulphuric acid, dilute to about 100 c.c., and titrate with the dichromate solution in the manner described in the preceding paragraph. As the concentration of the dichromate is approximately known, no drops of the ferrous solution need be removed for testing until the titration is almost complete.

An alternative method is as follows:—Weigh (to the nearest centigram) about 4 grams of the ferrous salt, transfer to a standard 100 c.c. flask containing about 25 c.c. of dilute sulphuric acid, and, after the salt has dissolved, make up to the mark. Take 25 c.c., add about 20 c.c. of dilute sulphuric acid, dilute to about 100 c.c., and titrate.

(2) If iron wire is to be used as standard, a weighed quantity is dissolved in acid by the method given on p. 93, in order that no oxidation of the ferrous salt may take place prior to titration. The “apparent” percentage of iron in the wire must be known (see p. 93).

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE OR DICHROMATE SOLUTIONS.

Titration with Permanganate in Presence of Hydrochloric Acid.—The determination of iron by volumetric methods may be made with either a standard permanganate or a standard dichromate solution. If the ferrous salt solution contains no hydrochloric acid, there is little to choose between the two methods in point of accuracy, but the permanganate titration is certainly the more convenient. If the solution contains hydrochloric acid or any chloride, it cannot be accurately titrated with permanganate unless precautions are taken, because the hydrochloric acid (even when cold and dilute) is oxidised by permanganate in presence of a ferrous salt, chlorine is liberated, and a serious error results. Another source of error is that the end-point of the titration is unsatisfactory on account of the yellow colour of the ferric chloride that is formed.

It is better to avoid a permanganate titration if the ferrous salt solution contains hydrochloric acid, although it is possible to overcome the difficulty almost entirely by adding sufficient phosphoric acid to keep the solution colourless until the end-point is reached. From 5 to 10 grams of glacial phosphoric acid are dissolved in about 20 c.c. of water and, in case any traces of reducing substances are present, potassium permanganate is cautiously added until the solution is tinged faintly pink. This solution is added to the ferrous chloride solution and the mixture is then titrated *very slowly* with the permanganate. If any brown or yellow colour is noticed, insufficient phosphoric acid has been added and the titration will be inaccurate.

Iron in Iron Wire.

Commercial iron is not chemically pure, although the amount of impurity in some varieties of iron is very small. As determined by volumetric methods, commercial iron sometimes appears to contain more than 100 per cent. of pure iron. This is due to the presence of impurities (carbides, etc.) that have a greater reducing action when dissolved in acid than an equal weight of pure iron.

The determination of the "apparent" percentage of iron in iron wire is made as follows:—Remove any trace of rust from some fine-drawn, soft iron wire ("flower wire") by means of emery cloth, and then clean the wire with filter paper. Weigh accurately about 0.6 gram of the wire and place it in a 200 c.c. flask fitted with a rubber stopper and bent tube (Fig. 33). The bent tube should dip into a sodium carbonate solution contained in a beaker. Pour about 10 c.c. of sodium carbonate solution into the flask in order that carbon dioxide will fill the flask when acid is added.

Dilute 10 c.c. of concentrated sulphuric acid by pouring it into 20 c.c. of water, and pour this mixture into the flask.

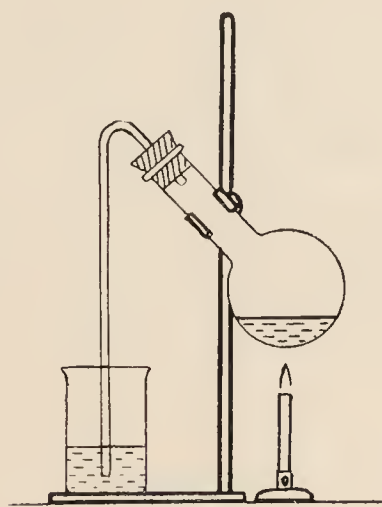


FIG. 33.

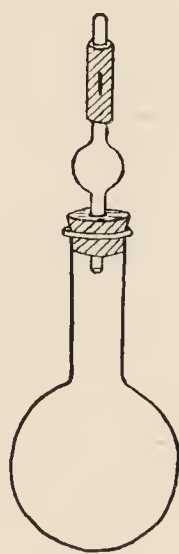


FIG. 34.

Replace the cork securely, and warm gently until all the iron has dissolved. (Minute particles of carbon sometimes remain undissolved.) Allow the solution to cool; meanwhile some of the sodium carbonate will pass into the flask and, by interaction with the acid, yield carbon dioxide. The solution is thereby protected from oxidation by the air. When nearly cold, detach the flask from the cork and tube, and hold it under the tap until cold.

Pour the solution into a standard 100 c.c. flask, rinse the original flask several times, and dilute the solution to the graduation mark. Mix the contents of the flask thoroughly, and titrate portions of 25 c.c. with standard permanganate or dichromate.

Alternative Method.—The solution of the iron wire may be prepared in a flask fitted with a Bunsen valve (Fig. 34).

This consists of a narrow rubber tube closed with a short piece of glass rod; a longitudinal slit in the rubber allows gas to escape outwards, but prevents any ingress of air. The procedure is otherwise identical with that already described.

Calculate the percentage of iron in the wire, assuming that the reducing action of the solution is due only to ferrous sulphate.

Iron in Ferrous and Ferric Compounds.

If the iron is wholly present in the ferrous condition, it is determined by direct titration with standard permanganate or dichromate, as described under standardisation by means of ferrous ammonium sulphate (pp. 79 and 91).

If the iron is present, wholly or partly, as ferric salt, it must be reduced to the ferrous state before titration (see, however, p. 134). The common methods of reduction are:—

- (1) With zinc and acid (this method can only be used in conjunction with permanganate, as zinc salts interfere with the dichromate titration);
- (2) With sulphur dioxide;
- (3) With hydrogen sulphide;
- (4) With stannous chloride.

As the reducing agents themselves also reduce permanganate or dichromate solutions, any excess of the reducing agent must be removed before the titration. If the solution is to be titrated with standard permanganate, phosphoric acid must be added if hydrochloric acid or a chloride is present (see p. 92).

Exercise.—Determine the percentage of iron in iron alum [ammonium ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$], using the various methods of reduction described below, and compare the results.

Dissolve about 12 grams (weighed to the nearest centigram) of iron alum in water to which 25 c.c. of dilute sulphuric acid has been added. Dilute in a standard flask to 250 c.c. and use 25 c.c. for each determination.

Reduction with Zinc.—To 25 c.c. of the iron alum solution contained in a conical flask, add 25 c.c. of water, 10 c.c. of concentrated sulphuric acid and 10 grams of

“pure,” granulated zinc (see below). Warm *gently* and allow the reaction to continue until the solution appears quite colourless, and then test for ferric salt:—Place a drop of potassium thiocyanate solution on a white porcelain surface, such as a crucible lid, and then bring into contact with the drop a *trace* of the iron solution which has been withdrawn from the flask by means of a *thin* glass rod or a capillary tube; a red coloration—it may be only a mere tinge—indicates that reduction is incomplete, *i.e.* that ferric salt is still present.

After the reduction is complete, allow the action to continue until *almost* the whole of the zinc has disappeared, additional sulphuric acid being added, if necessary, to effect this. (An insoluble residue, chiefly lead, nearly always remains.) Filter through a small plug of glass wool into a flask containing 25 c.c. of dilute sulphuric acid. Rinse the original flask and any undissolved residue several times with dilute sulphuric acid, pouring this also through the filter, and wash the latter carefully with water. Titrate the solution with standard permanganate.

Since the best commercial zinc invariably contains at least a trace of iron, a “blank” determination must be carried out in order to find the correction for that impurity. In the “blank” determination, the same quantities of zinc and sulphuric acid are used but the ferric salt is omitted, and, after the zinc has *almost* completely disappeared, the solution is filtered and titrated with the permanganate. With good zinc, only a few drops of permanganate should be required in the “blank,” and an equal amount must be deducted from the volume of permanganate required for the titration of the reduced ferric salt solution.

Reduction with Zinc in a Jones “Reductor.” — The reduction of a ferric salt with zinc may be more rapidly accomplished by using a Jones “reductor” (Fig. 35), in which a large surface of zinc is exposed to the solution. The part A to B of the reductor is about 25 cm. long and 2 cm. wide,

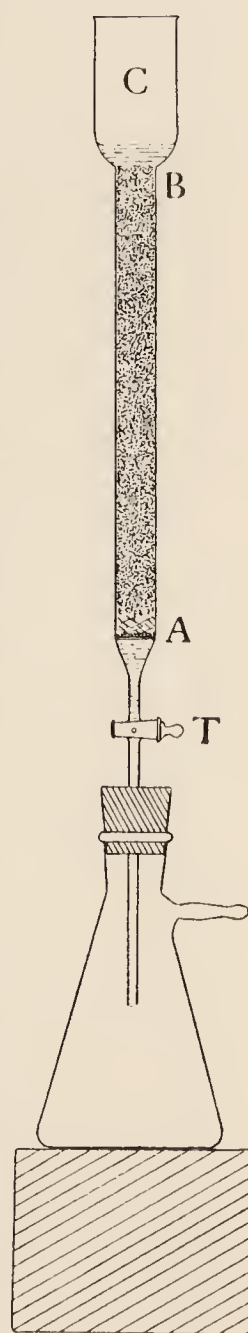


FIG. 35.

and is filled with amalgamated zinc granules. The cup C is about 8 cm. long and 4 cm. wide. A tap is provided at T. The reductor is held in a clamp and is fitted into a 400 c.c. filter-flask which rests on a block of wood. By taking away the block, the flask can be removed without disturbing the rest of the apparatus.

The amalgamated zinc is prepared as follows:—In a large beaker or basin cover 250 grams of zinc granules (through 10- on 20-mesh screen) with dilute (normal) hydrochloric acid, stir for a moment, and then add 150 c.c. of mercuric chloride solution (0.2N). Stir vigorously until hydrogen ceases to be evolved (about two minutes). Decant the solution and wash the zinc thoroughly by decantation—finally with distilled water. After draining the water as completely as possible, dry the zinc on a clock-glass in the steam-oven.

Drop a perforated porcelain disc into the tube at A, and place about 0.3 gram of glass wool on the disc. Then pour into the tube about 30 milligrams of Gooch crucible asbestos mixed with water and drain the water by gentle suction. Fill the part A to B of the tube with the amalgamated zinc.

Prepare approximately 0.2N sulphuric acid by diluting 25 c.c. of the dilute acid (4N) to 500 c.c. Run about 200 c.c. of this acid, followed by 100 c.c. of water, through the reductor, using gentle suction, care being taken that no air is allowed to enter the zinc column—a precaution that must always be observed in using the reductor. Empty and rinse the filter-flask. The apparatus is now ready for use.

“Blank” determination.—Since the zinc is seldom entirely free from iron, a “blank” determination must be made as follows:—Run 100 c.c. of 0.2N sulphuric acid, followed by 100 c.c. of water, through the reductor, care being taken to close the tap T before the surface of the zinc is exposed to the air. Detach the flask, add 10 c.c. of dilute (4N) sulphuric acid, and titrate with standard permanganate. With good zinc only 1 to 2 drops (less than 0.1 c.c.) of decinormal permanganate should be required. Repeat the determination to make sure that the “blank” titration requires a constant amount.

Reduction of the ferric salt solution.—Measure 25 c.c. of

the iron alum solution into a small beaker and add an equal volume of water. (The concentration of acid in this solution is about 0.2N.) Pour the solution into the cup of the reductor, open the tap, and regulate the suction so that about two minutes are required for the 50 c.c. of solution to pass through the column. Close the tap before the zinc is exposed. Rinse the beaker with 50 c.c. of 0.2N acid and run this also through the reductor. Finally rinse the beaker and the cup C with water—using 100 c.c. in all—this water also being drawn through the zinc column. Close the tap before the cup is quite empty. Remove the filter-flask, add 10 c.c. of dilute (4N) sulphuric acid, and titrate the solution with standard permanganate. Deduct the correction indicated in the “blank” determination.

Reduction with Sulphur Dioxide.—If the solution is acid, it must be made nearly neutral by adding ammonia until a slight permanent precipitate of ferric hydroxide forms. The reducing agent is then added, either in the form of sulphurous acid solution or a sulphite, or by passing a current of sulphur dioxide from a siphon of the liquefied gas through the cold solution. The solution after the reducing agent is added, must be *slightly acid* to litmus; if it is alkaline, no reduction takes place. The excess of sulphur dioxide is removed by adding acid and passing a current of carbon dioxide through the boiling solution.

To 25 c.c. of the iron alum solution, add ammonia until a slight permanent precipitate forms, and then 25 c.c. of sulphurous acid solution. Boil the mixture for ten minutes. Now add about 20 c.c. of dilute sulphuric acid, heat until boiling again, and pass a fairly rapid current of carbon dioxide through the boiling solution until the sulphur dioxide is completely expelled (about twenty minutes). Cool the solution—without interrupting the gas current—by placing the flask in a basin of water. Rinse the gas-delivery tube and remove it. Titrate the solution with either standard permanganate or dichromate.

Reduction with Hydrogen Sulphide.—By passing a current of hydrogen sulphide through a solution of a ferric salt, sulphur is precipitated and the ferric salt is completely reduced to the ferrous state. The solution should con-

tain about 2 per cent. by volume of concentrated sulphuric acid. The excess of hydrogen sulphide is removed by passing a current of carbon dioxide through the boiling solution.

Add 10 c.c. of dilute sulphuric acid to 25 c.c. of the iron alum solution contained in a 200 c.c. flask. Dilute to about 50 c.c., pass hydrogen sulphide into the cold solution for five minutes, then heat until boiling, and continue the current of gas until the precipitated sulphur has coagulated. Allow the solution to cool somewhat without interrupting the gas current, and then filter into another flask, rinsing the original flask and washing the filter carefully. Dilute the solution, if necessary, to about 100 c.c., and pass a fairly rapid current of carbon dioxide through the boiling solution until hydrogen sulphide cannot be detected in the escaping gas by means of lead acetate paper.¹ Cool the solution—without interrupting the gas current—and titrate the solution with standard permanganate or dichromate.

Reduction with Stannous Chloride.—Stannous chloride is added to the ferric salt solution containing hydrochloric acid until the colour is discharged. The excess of the stannous chloride is destroyed by adding mercuric chloride, and the solution is then titrated with standard dichromate.

The stannous chloride solution may be prepared by dissolving 3 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 c.c. of concentrated hydrochloric acid, and diluting to about 100 c.c.²

To 25 c.c. of the iron alum solution contained in a 300 c.c. beaker, add 5 c.c. of concentrated hydrochloric acid, heat until boiling, and then run in the stannous chloride drop by drop from a burette until the yellow colour of the solution is just discharged. A slight excess (one or two drops) of the stannous chloride is essential, but a large excess must be carefully avoided. Cool the solution, dilute to 150 c.c., and then add (rapidly, and while stirring) about 10 c.c. of saturated mercuric chloride solution. A very slight, *white* precipitate should form. If no precipitate appears, insufficient

¹ If the solution is clear, ten minutes is usually sufficient, but so long as it is milky (on account of sulphur in suspension) a minute trace of hydrogen sulphide will always be found in the escaping gas.

² The side-shelf reagent is suitable, if it has been recently prepared.

stannous chloride has been added, whilst a grey or black precipitate shows that too much stannous chloride was used; in either case the experiment must be rejected.

Titrate the turbid mixture with standard dichromate, or add phosphoric acid (see p. 92) and titrate with permanganate.

Total Iron in a Mineral.

(Hæmatite; Magnetite; Bog Iron Ore; etc.)

If the ore is in large pieces, a representative sample is crushed (without grinding) in a clean, steel percussion mortar. The coarse powder is then finely ground in an agate mortar. Iron ores sometimes dissolve very slowly in acid unless they are reduced to an impalpable powder.

Dissolving the Ore.—Weigh accurately about 1 gram of the ore, or a larger quantity if the ore contains little iron. If the ore contains carbonaceous matter (as is often the case), weigh it in a porcelain crucible, and heat to dull redness for ten minutes.

Transfer the weighed portion of the ore, after ignition, to a 200 c.c. flask, and add 15 c.c. of concentrated hydrochloric acid. Warm on the steam-bath for some time, and then keep near the boiling-point of the acid until the undissolved residue, if any, is perfectly white. (Nothing is gained by boiling vigorously—this merely weakens the acid.)

If this treatment fails to extract all the iron from the ore, *i.e.* if the residue is still coloured, add to the hot liquid at intervals 1 to 2 c.c. of stannous chloride (avoiding excess); rapid solution usually follows in the case of a hæmatite ore. If excess of stannous chloride is inadvertently added, reoxidise the iron partially with a few drops of potassium permanganate.

When as much as possible of the ore has been brought into solution, and whether the residue is coloured or not, dilute with a little water, and filter into a 100 c.c. standard flask. Rinse the original flask and wash the filter carefully, first with dilute hydrochloric acid and then with water, using as little as possible. If the filtrate contains all the iron, cool, and make it up to 100 c.c.

If the insoluble residue is coloured, and therefore probably contains iron (provided organic matter was destroyed

by ignition), incinerate the filter paper together with the residue in a porcelain crucible (p. 152). Then add 2 to 3 grams of fused potassium hydrogen sulphate (pyrosulphate), heat cautiously, and keep the mixture fused until the dark specks of iron oxide have disappeared. Cool, place the crucible in a small porcelain basin, and dissolve the solid residue in the minimum quantity of dilute sulphuric acid. Filter if necessary (most of the silica remains undissolved), and receive the filtrate and rinsings in the flask containing the main solution of the ore. Dilute to 100 c.c.

Titration of the Solution.—Use 25 c.c. of the solution for each titration. If stannous chloride was used in the preparation of the solution, the reduction of the ferric salt must also be effected with stannous chloride; otherwise hydrogen sulphide or sulphur dioxide may be used as the reducing agent. After reduction, the solution may be titrated with either standard dichromate or permanganate. If standard permanganate is to be used, phosphoric acid must be added before the titration (*cf.* p. 92).

Methods for Refractory Oxides and Silicates.—The acid treatment described above will not always dissolve all the iron in the sample. The addition, from time to time, of a few crystals of potassium chlorate to the concentrated hydrochloric acid promotes the solution of refractory oxides such as magnetite. The same treatment also serves to oxidise any sulphides or carbonaceous matter the sample may contain. If potassium chlorate has been added, the solution should then be boiled for some time, or evaporated to a small volume, in order to free it from chlorine.

Natural silicates and artificial siliceous slags must be decomposed, as a rule, by fusing with sodium carbonate, or "fusion mixture," as described under silica (p. 253). If only the iron in the silicate is to be determined, it is not necessary to evaporate to dryness in order to remove the silica. The acid solution obtained after the fusion is treated as follows:—Warm the solution in a beaker, add a little bromine water and heat until boiling, in order to oxidise any ferrous salt. Precipitate the iron (together with aluminium, manganese, etc.) by adding ammonia in slight excess. Boil for a minute, allow the precipitate to settle, filter, transfer

the precipitate to the filter, and wash it thoroughly with hot water. By means of a jet of hot water, transfer the bulk of the precipitate from the filter to a beaker, and then place the beaker under the funnel. Dissolve the precipitate remaining on the filter by pouring through the funnel a hot mixture of 10 c.c. of concentrated hydrochloric acid and 10 c.c. of water. Wash the filter carefully, at first with hot dilute hydrochloric acid and then with hot water. Reduce with stannous chloride, and titrate with standard potassium dichromate.

Separate Determination of Ferrous and Ferric Iron in a Mineral.

Ferrous Iron.—The exact determination of ferrous iron in minerals is a very difficult operation. Reference may be made to Hillebrand's *Analysis of Silicate and Carbonate Rocks*, p. 189, for a description of the methods employed and the difficulties encountered.

Certain precautions are necessary in regard to the grinding, as it is found that considerable oxidation occurs if the sample is ground to a fine powder in the ordinary manner. A very fine powder is usually essential, and oxidation may be prevented by grinding *the weighed sample* under alcohol in an agate mortar. The alcohol is then allowed to evaporate spontaneously.

Solution must then be effected in absence of air. If the mineral dissolves in hydrochloric acid, the operation may be conducted in a flask which has been filled with carbon dioxide before the acid is added, and which is kept filled by passing a current of carbon dioxide into the flask until solution is complete. The solution is then cooled in an atmosphere of carbon dioxide, diluted if necessary, and titrated.

If the mineral does not dissolve readily in hydrochloric acid, it must be decomposed in absence of air by means of hydrofluoric acid in presence of sulphuric acid. (For details, see Hillebrand, *loc. cit.*)

Ferric Iron.—The total iron is then determined by one of the methods already described, and the difference between the total iron and the ferrous iron gives the amount present in the ferric state.

Iron in Black Ink.

Black inks often owe their colour to iron-tannin compounds. The organic matter must be destroyed before the iron in the ink can be determined.

Weigh (to the nearest centigram) 10 grams of ink in a 100 c.c. porcelain basin. Evaporate to dryness on the steam-bath, and then heat the residue and burn away the organic matter at as low a temperature as possible. Dissolve the ash by warming with about 10 c.c. of concentrated hydrochloric acid, adding, if necessary, a few drops of stannous chloride at intervals. Transfer the solution to a 300 c.c. beaker, heat to the boiling-point, and reduce the ferric salt with stannous chloride. Dilute to about 150 c.c., add excess of mercuric chloride, and titrate with standard dichromate.

Express the result in grams of Fe_2O_3 per 100 grams of ink.

Iron and Chromium in Chrome Iron Ore.

Decomposition of the Ore.—Grind the ore *very finely* in an agate mortar. Weigh accurately about 0.5 gram, transfer to a nickel crucible, and mix thoroughly by means of a thin glass rod with about 4 grams of sodium peroxide. Heat the crucible gently with a very small Bunsen flame until the contents melt, and then keep the mixture at low redness for about ten minutes. Remove the flame until a crust forms, then add another gram of sodium peroxide, and heat again to low redness for about five minutes.

Place the crucible, after cooling, in a porcelain basin, add about 50 c.c. of water, and warm until the yellow mass has dissolved. Remove the crucible and rinse it. If the solution is purple in colour, add a little more sodium peroxide, and then boil the solution in the covered basin until the excess of sodium peroxide is *completely* decomposed. In order to neutralise the large excess of sodium hydroxide in the solution, add about 5 grams of ammonium carbonate and boil again. Filter and wash the precipitate thoroughly. Determine the iron in the precipitate and the chromium in the filtrate.

Iron.—Dissolve the precipitate by pouring hot hydrochloric acid (equal volumes of concentrated acid and water)

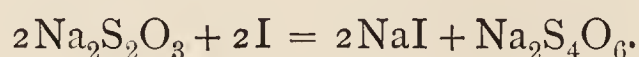
into the filter, and receive the solution in a 300 c.c. beaker. Wash the filter with hot dilute hydrochloric acid and then with hot water. (If any dark-coloured residue remains, it must be fused again with sodium peroxide.) Reduce the ferric salt in the solution with stannous chloride, and titrate with standard dichromate.

Chromium.—Add dilute sulphuric acid to the filtrate until it is acid (orange-yellow), and then add 25 c.c. more acid. Allow the solution to cool; then reduce the dichromate by adding a known excess of ferrous ammonium sulphate, as follows:—Place several grams of the ferrous salt in a weighing-bottle and weigh the bottle and contents; then add the salt to the chromate solution gradually, while stirring, until it is free from orange-yellow colour, and until a small drop of the solution gives a blue coloration with a drop of freshly prepared potassium ferricyanide solution.

Titrate the excess of ferrous salt in the solution with standard dichromate. Also weigh the weighing-bottle again, and thus determine the weight of ferrous ammonium sulphate used.

Standard Sodium Thiosulphate and Standard Iodine

SODIUM thiosulphate is useful in volumetric analysis mainly on account of the manner in which it interacts with iodine, viz. :—



The process may be used for the determination of iodine itself and all substances (mainly oxidising agents) that will liberate iodine from potassium iodide, and is therefore capable of wide application.

Standard iodine solution is used as an oxidising agent for the determination of easily oxidisable substances, such as sulphurous acid, arsenic (as sodium arsenite), and tin (as stannous chloride). Sometimes the standard iodine and thiosulphate solutions are used in conjunction.

In iodometric titrations a dilute solution of starch is generally used as an indicator. Starch solution is a very sensitive reagent for minute traces of iodine, provided a soluble iodide is also present—a condition that is fulfilled in most titrations without special precautions.

DECINORMAL SODIUM THIOSULPHATE.

(N/10 solution contains 24.82 grams of $\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$ per litre.)

Since the molar weight (248.2 grams) of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$, is equivalent to 127 grams of iodine (compare the above equation), a solution that contains 24.82 grams of the salt per litre is described as a decinormal solution. The so-called "pea crystals" of photographic "hypo" are usually very pure, but when the salt is dissolved in ordinary distilled water it suffers slight decomposition

and the concentration of the solution slowly alters. The solution keeps better if a small quantity of sodium carbonate is added to it. An approximately decinormal solution is therefore prepared by dissolving about 25 grams of the crystals, together with 0.2 gram of sodium carbonate, in a litre of water, and the solution is standardised as described below.

Preparation of the Starch-Indicator Solution.—Mix 1 gram of “soluble starch” with a little cold water, pour the mixture into 200 c.c. of almost boiling water, and boil for about one minute. After cooling, the solution is ready for use. If “soluble starch” is not available, grind 1 gram of ordinary starch with a little cold water, pour the mixture slowly into 200 c.c. of boiling water and boil for two minutes. Set aside for a few hours (or overnight) and decant the clear liquid. Starch solution will not keep in good condition for more than about two days unless it is sterilised, *e.g.* by adding either 5 c.c. of dilute hydrochloric acid or 2 milligrams of mercuric iodide to the above quantity.

Standardisation of Sodium Thiosulphate with Pure Iodine.—Commercial iodine is often impure, and should be ground up with a little solid potassium iodide and resublimed before use.¹ On account of its volatility, iodine cannot be accurately weighed in the ordinary manner, and the following special method must therefore be adopted.

In a weighing-bottle place about 2 grams of pure potassium iodide with 10 *drops* of water, and weigh accurately. Add 0.3 to 0.4 gram of pure iodine, replace the stopper at once, and weigh again. This gives the weight of the iodine. When the iodine has dissolved, wash it rapidly into a flask containing about 1 gram of potassium iodide in about 200 c.c. of water, and titrate *at once* with the sodium thiosulphate solution. When the iodine solution becomes very pale yellow in colour, add about 2 c.c. of starch solution and continue the titration until the blue colour just disappears.

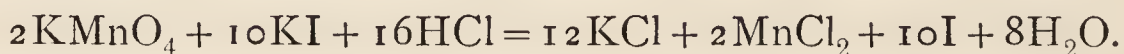
¹ A small quantity of pure iodine may be prepared as follows:—Grind together in a mortar about 2 grams of iodine with about 0.2 gram of potassium iodide. Place the mixture in a small porcelain basin, cover with a clock-glass, and heat gently. Regulate the heat so that the iodine sublimes slowly on to the clock-glass.

Repeat the process with another weighed quantity of iodine and from the results calculate the normality of the thiosulphate solution.

Notes.—A solution of iodine in potassium iodide loses iodine somewhat readily on exposure in an open vessel; for that reason it is advisable to carry out the titrations in conical flasks rather than in beakers, and with as little delay as possible.

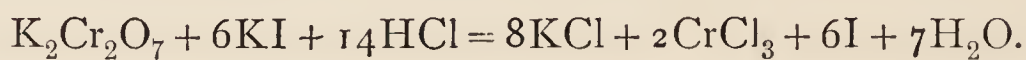
The starch solution must not be added until near the end of the titration. If the volume of the iodine solution is not large, it is possible to complete the titration without using starch—except in artificial light.

Standardisation of Sodium Thiosulphate with Potassium Permanganate.—If potassium permanganate is added to an acid solution of potassium iodide, the permanganate is reduced and an equivalent amount of iodine is liberated. A solution of sodium thiosulphate can therefore be standardised by titrating the iodine liberated from potassium iodide by a measured volume of standard potassium permanganate solution.



Dissolve about 2 grams of potassium iodide in 10 c.c. of water, and add 10 c.c. of dilute hydrochloric acid. To this mixture add 25 c.c. of standard (decinormal) potassium permanganate, dilute to about 200 c.c., and titrate the liberated iodine *at once* with the thiosulphate solution as described above.

Standardisation of Sodium Thiosulphate with Potassium Dichromate.—When potassium dichromate is added to an acid solution of potassium iodide, iodine is liberated according to the equation—



If a standard (decinormal) solution of potassium dichromate is available, it may be used for the standardisation of the thiosulphate solution, the procedure being the same as with standard permanganate (see above). Instead of a standard solution, weighed quantities of potassium dichromate may be used.

Dissolve about 2 grams of potassium iodide in 10 c.c. of

water and add 10 c.c. of dilute hydrochloric acid. To this solution add 0.12 to 0.14 gram (accurately weighed) of potassium dichromate, dilute to about 200 c.c., and titrate the liberated iodine at once with the thiosulphate solution, using starch as indicator. At the conclusion of this titration the solution is green in colour, on account of the chromic chloride present. The colour change at the end-point—from blue to light green—is nevertheless easily observed if the solution is diluted to at least 200 c.c.

The gram-equivalent of potassium dichromate is 49.03.

Standardisation of Sodium Thiosulphate with Pure Copper.—This is described on p. 110.

DECINORMAL IODINE.

(N/10 solution contains 12.69 grams per litre.)

Iodine is almost insoluble in water, but dissolves in a solution of potassium iodide. It is very volatile, and in both the preparation and use of a standard iodine solution, precautions are necessary to prevent loss by volatilisation. Commercial iodine is usually impure, and, even if pure iodine is available, it is difficult (on account of its volatility) to prepare an accurate standard solution by weight. It is preferable, therefore, to prepare an approximately decinormal solution from commercial (B.P.) iodine, and standardise it by means of arsenious oxide, or with a standard sodium thiosulphate solution.

On a rough balance weigh 6.4 grams of powdered iodine and introduce it into a 500 c.c. standard flask. Add 10 to 12 grams of potassium iodide (free from iodate), and *not more than 20 c.c. of water*. Shake until all the iodine has dissolved, and then dilute to the graduation mark. Iodine dissolves quickly in a concentrated potassium iodide solution, but very slowly in a dilute solution, and much time will therefore be wasted if the solution is diluted before all the iodine has dissolved.

Standardisation with Arsenious Oxide.—The oxidation of arsenious oxide by iodine may be represented by the equation—



The reaction is reversible, but the oxidation is quantitative if the hydriodic acid is neutralised as it is formed. Neither sodium hydroxide nor sodium carbonate may be used for this purpose, since they interact with iodine, but sodium bicarbonate introduces no appreciable error if the solution is saturated with carbon dioxide. The hydrolysis of the bicarbonate is then very slight, and the solution at the end of the titration is approximately neutral.

The arsenious oxide, unless it is known to be pure, must be purified by resublimation, or in the following way:—Dissolve 10 grams of the commercial oxide in 50 c.c. of warm concentrated hydrochloric acid. Add 100 c.c. of water and set the solution aside overnight. Filter the crystals of arsenious oxide that separate, wash them with a little cold water, and dry in a desiccator.

Weigh accurately in a small porcelain basin about 1.25 gram of pure arsenious oxide. Add 10 c.c. of sodium hydroxide solution (bench reagent) and warm the basin on the steam-bath, stirring the mixture gently, until the oxide dissolves (about five minutes). Transfer the solution and the rinsings of the basin to a 250 c.c. standard flask, and add 20 c.c. of dilute hydrochloric acid. Then add about 8 grams of sodium bicarbonate (or 100 c.c. of a cold saturated solution), and dilute the solution to the graduation mark.

Place the arsenite solution in a burette. Measure 25 c.c. of the iodine solution into a conical flask (not a beaker). Run the arsenite solution slowly down the side of the flask (in order to avoid loss of carbon dioxide), and mix occasionally by gentle rotation. When the iodine solution becomes very pale yellow, add 2 c.c. of starch solution and continue the titration until the blue colour just disappears. The reaction is sometimes a little slow at the end-point, and an interval of twenty seconds or so should be allowed between each of the last two or three drops of the arsenite solution added.

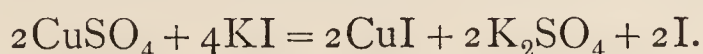
The gram-equivalent of arsenious oxide is 49.5.

Note.—The standard sodium arsenite solution may be used also for the determination of the available chlorine in bleaching powder (see p. 133).

ANALYSES INVOLVING THE USE OF STANDARD IODINE AND STANDARD THIOSULPHATE.

Copper.

When a copper salt is mixed with a solution of potassium iodide, cuprous iodide is precipitated and iodine is liberated :



The amount of copper can therefore be found by titration of the free iodine. According to the equation, 1 gram of copper requires 5.22 grams of potassium iodide, but in practice a considerable excess of the latter is necessary; if the solution to be titrated contains about 0.15 gram of copper—requiring about 25 c.c. of standard (decinormal) thiosulphate—about 2 grams of potassium iodide should be added.

Exercise.—The copper in a bronze or “nickel” coin, or in brass, may be determined by this method.

Clean a halfpenny with emery cloth, and cut it into four approximately equal pieces. Weigh one of the pieces accurately. Place the weighed piece in a 200 c.c. conical flask, add 5 c.c. of water and 5 c.c. of concentrated nitric acid, and warm on the steam-bath until the alloy has dissolved (about twenty minutes). The small white residue of stannic oxide need not be filtered off, since it in no way interferes with the analysis.

It is essential that the solution to be titrated should contain no nitrite and no acid other than acetic acid, and the following procedure must be closely adhered to. Dilute the solution with 25 c.c. of water and boil it briskly for two minutes in order to expel oxides of nitrogen. Rinse the neck and side of the flask with a little water, and then add about 0.5 gram of urea (in order to destroy traces of nitrous acid). Neutralise the nitric acid by adding ammonia (about 15 c.c.) until a bluish-white precipitate forms. Then add acetic acid (about 5 c.c.) more than sufficient to redissolve the precipitate. Cool, and dilute the solution to 250 c.c. in a standard flask.

In a 200 c.c. conical flask, dissolve 2 grams of potassium iodide in 20 c.c. of water, and add 25 c.c. of the copper solu-

tion. (Cuprous iodide is nearly white, but the free iodine colours the mixture brown.) Titrate the mixture with standard sodium thiosulphate until the brown colour becomes faint; then add 2 c.c. of starch solution, and continue the titration until the mixture loses the last trace of a grey-blue tinge and appears almost white. The end-point is quite sharply defined. After reading the burette, however, it will be found advantageous—until some experience has been gained—to add a few additional drops of the thiosulphate and to keep the mixture as a guide for a second titration.

The reappearance of the blue colour soon after the titration is apparently finished indicates that the solution contains nitrite, or that insufficient potassium iodide was added—in short, that the above directions have not been carefully followed.

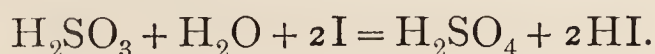
Calculate the percentage of copper in the coin. One litre of normal thiosulphate corresponds to 63.57 grams of copper.

Standardisation of Sodium Thiosulphate with Pure Copper.—If a solution of sodium thiosulphate is to be used mainly for the determination of copper, it is best to standardise it in the following manner:—Weigh accurately about 0.15 gram of pure (electrolytic) copper foil. Place it in a 200 c.c. conical flask, add 1 c.c. of water and 1 c.c. of concentrated nitric acid, and warm the flask on the steam-bath until the copper has dissolved. Following the method detailed in the preceding paragraph, dilute the solution with 25 c.c. of water, boil briskly for two minutes, and add 0.5 gram of urea. Then add ammonia until a precipitate forms, and redissolve the precipitate in acetic acid. Cool, add 2 grams of potassium iodide, and titrate the mixture with the thiosulphate.

Alternative Method.—Weigh accurately about 2.5 grams of copper sulphate (A.R.). Wash it into a 100 c.c. standard flask and dissolve in water. Add about 1 c.c. of ammonia and 5 c.c. of acetic acid, and dilute the solution to the mark. Measure 25 c.c. of the solution into a conical flask, add 2 grams of potassium iodide, and titrate with the thiosulphate solution. (One litre of normal thiosulphate corresponds to 249.7 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.)

Sulphurous Acid and Sulphites.

Sulphurous acid in dilute aqueous solution is oxidised by iodine to sulphuric acid according to the equation—



The alkali sulphites are oxidised to sulphates in a similar manner.

The sulphite solution is run into a measured excess of iodine (not *vice versa*), with constant stirring, and the residual iodine is then titrated with standard thiosulphate. If the iodine is run into the sulphite solution, the reaction takes place in accordance with the above equation only when the sulphite solution is very dilute (about centinormal).

Exercise.—Determine the percentage of Na_2SO_3 in a sample of commercial sodium sulphite crystals. Weigh accurately from 2.5 to 2.8 grams of the crystals, dissolve in water, and dilute to 250 c.c. in a standard flask.

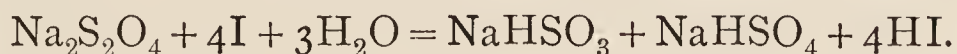
Measure 25 c.c. of decinormal iodine into a flask, add 5 c.c. of dilute hydrochloric acid, dilute to about 100 c.c., and add slowly 25 c.c. of the sulphite solution. Titrate the excess of iodine with standard thiosulphate.

Sodium Hydrosulphite.

Sodium hydrosulphite (sometimes called sodium hypsulphite), $\text{Na}_2\text{S}_2\text{O}_4$, is decomposed by formaldehyde to form two “addition” compounds derived from sulphurous acid and (true) hyposulphurous acid or sulphonylic acid, H_2SO_2 .



Sodium formaldehyde-bisulphite does not interact with iodine in neutral or acid solution, but sodium formaldehyde-sulphonylate is oxidised, the sulphonylate being converted into sulphate. The essential change is given by the equation



The molar weight (174 grams) of sodium hydrosulphite requires 4×127 grams of iodine, and therefore 1 c.c. of normal iodine is equivalent to 0.0435 gram of sodium hydrosulphite. A solution of sodium hydrosulphite combines very

rapidly with oxygen, and exposure to air must be avoided as far as possible when preparing it for analysis.

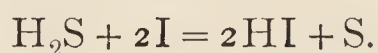
Procedure.—In a 250 c.c. graduated flask (the neck of which has been cut off to within 1 inch of the graduation mark) mix 5 c.c. of 40 per cent. formaldehyde with 200 c.c. of air-free water (recently boiled and rapidly cooled water). While rotating the flask, introduce 2 grams of the hydrosulphite through a dry funnel with a short stem. Rinse the funnel with water and without delay dilute the solution to the graduation mark. Stopper the flask and mix the contents thoroughly by repeatedly inverting the flask during five minutes. (Mixing is slow on account of the small air space.)

In a 300 c.c. conical flask place 100 c.c. of water and 50 c.c. of decinormal iodine, and then add 25 c.c. of the hydrosulphite solution. Set aside for two minutes, and then titrate the excess of iodine with standard sodium thiosulphate solution, using starch as indicator.

A correction of about 1 per cent. is necessary for the unavoidable loss of hydrosulphite due to oxidation by air.

Hydrogen Sulphide.

Hydrogen sulphide interacts with iodine in aqueous solution according to the equation—



A measured volume of the hydrogen sulphide solution is run into excess of decinormal iodine, and the excess of the latter is then titrated with standard thiosulphate.

If the concentration of the hydrogen sulphide solution is more than about 0.025 normal, the precipitated sulphur encloses a portion of the iodine which is thereby protected from interaction with the thiosulphate; the titration is then inaccurate. Accordingly, after making a preliminary titration, the hydrogen sulphide solution must be diluted in a standard flask with air-free water in such proportions that 10 c.c. of decinormal iodine will oxidise about 40 c.c. of the sulphide solution.

Hydrogen Sulphide in Mineral Water.—In order to determine the amount of hydrogen sulphide in mineral

waters, take a measured volume, say 5 c.c., of decinormal (or centinormal) iodine, add starch solution and 2 grams of potassium iodide, and pour in the water from a measuring cylinder until the blue colour is discharged. Titrate back with decinormal (or centinormal) iodine. A correction is necessary for the amount of iodine required to produce a blue colour in absence of hydrogen sulphide. In order to determine this, add starch solution and 2 grams of potassium iodide to a quantity of distilled water equal in volume to that of the mineral water used, and titrate with the iodine.

Exercise.—Determine the solubility of hydrogen sulphide in water at room temperature.

Dioxides, Chromates, Chlorates, etc.

Substances that oxidise hydrochloric acid with evolution of chlorine may be accurately determined in the following manner. The method is specially useful for dioxides such as lead dioxide, red lead, and manganese dioxide, and as an illustration the determination of manganese dioxide in pyrolusite is described.

Valuation of Pyrolusite.—Manganese dioxide interacts with hydrochloric acid according to the equation—



If the chlorine is passed into potassium iodide solution, it liberates an equivalent amount of iodine which may be determined by titration with standard sodium thiosulphate solution.

Reduce some pyrolusite to a fine powder by thorough grinding. In a small weighing-tube ($\frac{1}{2}$ inch wide and $\frac{3}{4}$ inch long) weigh accurately from 0.10 to 0.15 gram of the powder, and introduce the tube and contents into a 200 c.c. distillation flask (Fig. 36).

Fit the flask with a cork and glass tube, so arranged that a current of carbon dioxide from a Kipp apparatus can be passed into the flask and through the solution that is to be boiled in it. Connect the bent side-tube of the flask with a U-tube which contains 2 grams of potassium iodide dissolved in just sufficient water to fill the bend of the tube. As a precaution against incomplete absorption, connect with the

U-tube a tube full of glass beads wetted with potassium iodide solution. Place the **U-tube** in a basin of cold water.

When the apparatus is ready, pour 10 c.c. of water and 20 c.c. of concentrated hydrochloric acid into the flask, and replace the cork at once. Heat the mixture very gently so that chlorine is slowly evolved. Gradually increase the temperature and finally heat until boiling, and pass a slow current of carbon dioxide through the boiling solution until all the chlorine is driven out of the flask (about ten minutes as a rule). In order to prevent the iodine and potassium

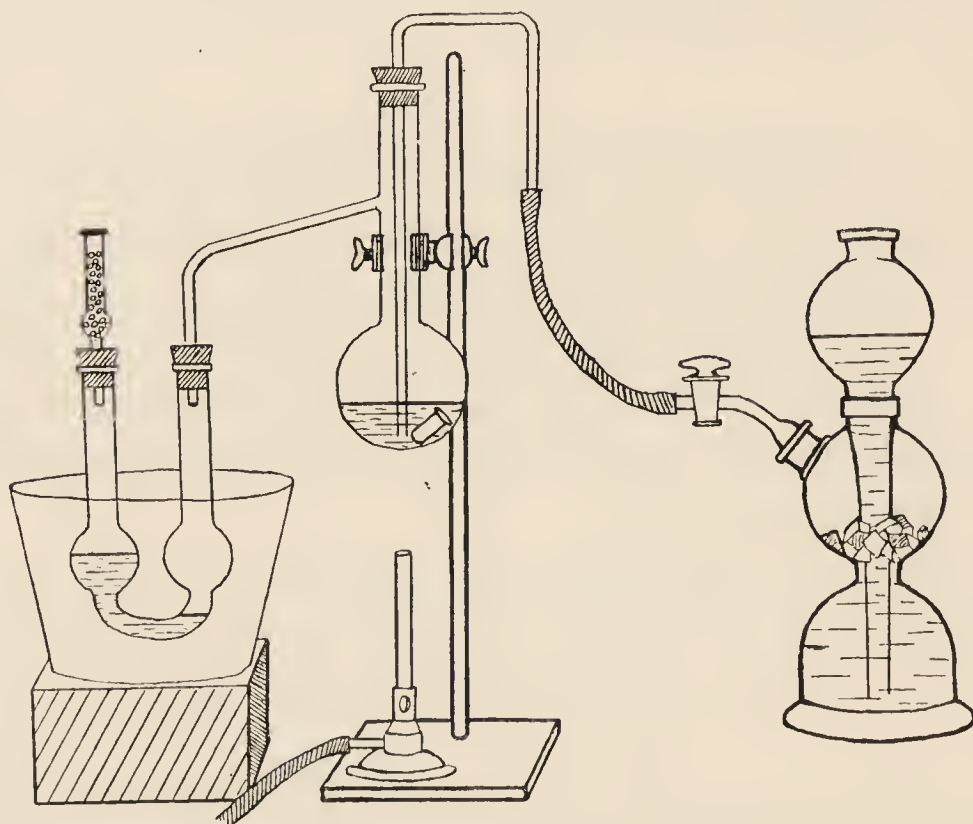


FIG. 36.

iodide solution from passing back into the flask, increase the current of carbon dioxide immediately the heating is stopped. (As pyrolusite invariably contains iron, the solution in the flask remains yellow at the end of the operation.)

Disconnect the absorption tube, wash the iodine and potassium iodide solution into a flask, and titrate at once in the usual manner with sodium thiosulphate.

Calculate the percentage of MnO_2 in the sample.

Lead Dioxide. — The lead dioxide is mixed with a solution containing hydrochloric acid, potassium iodide, and a large excess of sodium chloride. The lead dioxide is converted into lead iodide which dissolves in the excess

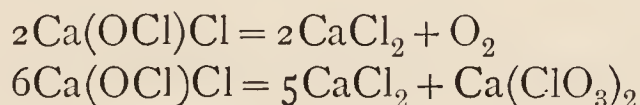
of sodium chloride, and an equivalent amount of iodine is liberated.



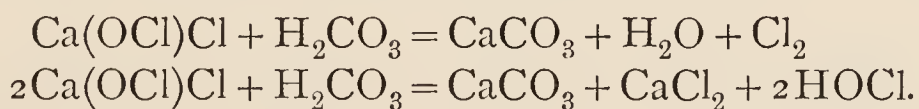
Place in a stoppered bottle 100 c.c. of water, 20 c.c. of concentrated hydrochloric acid, 1 gram of potassium iodide, and 20 to 25 grams of sodium chloride. Add 0.25 gram of *finely powdered* lead dioxide (or 0.7 gram of red lead) and shake vigorously for about two minutes. Titrate the liberated iodine with decinormal thiosulphate. Calculate the percentage of PbO_2 (or Pb_3O_4) in the sample.

Available Chlorine in Bleaching Powder.

Bleaching powder may be regarded as a mixed salt, $\text{Ca}(\text{OCl})\text{Cl}$, H_2O . When treated with acid, the whole of the chlorine in this mixed salt, amounting to about 49 per cent., is liberated, and is therefore "available." The best commercial samples, however, seldom contain more than 36 to 38 per cent. of available chlorine. Bleaching powder decomposes slowly on keeping, with formation of calcium chloride and chlorate,

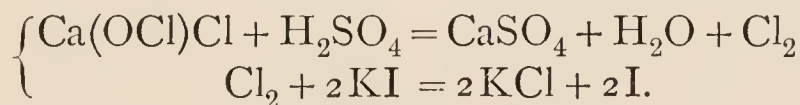


whilst exposure to atmospheric moisture and carbon dioxide results in loss of chlorine and hypochlorous acid,



The available chlorine thus diminishes on keeping, and is no longer equal to the total chlorine (see p. 131).

The amount of available chlorine may be determined by mixing a solution of the bleaching powder with excess of potassium iodide and adding acid. The reaction is—



The liberated iodine, which is equivalent to the available chlorine, is then titrated with standard thiosulphate. The procedure is as follows:—

Weigh accurately (in a stoppered weighing-bottle) about 2.5 grams of bleaching powder. Bleaching powder is not

completely soluble in water; in order to obtain a uniform sample, it must be so finely ground that the insoluble portion will remain for some time in suspension. Transfer the weighed sample to a glazed porcelain mortar, add 2 to 3 c.c. of water, and grind to a smooth paste. Add more water gradually, then transfer the mixture completely to a 250 c.c. standard flask and make up to the mark. Mix the contents of the flask by shaking, and repeat the shaking immediately before withdrawing each sample for titration.

Measure 25 c.c. of the mixture into a 200 c.c. flask, add about 1 gram of potassium iodide (10 c.c. of a 10 per cent. solution), and excess of acetic acid. Titrate the iodine with standard thiosulphate.

Alternative Method.—The available chlorine in bleaching powder may also be determined by means of standard sodium arsenite (see p. 133).

Total Arsenic in Commercial Arsenious Oxide.

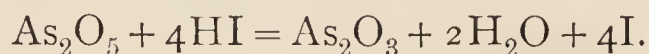
Commercial arsenious oxide often contains some arsenic oxide as impurity. The following method of analysis is applicable also to mixtures of arsenious and arsenic salts.

Determination of Arsenious Oxide.—The arsenious oxide may be determined by the process already described for standardising a solution of iodine by means of arsenious oxide.

Weigh accurately about 1.2 gram of a sample of the commercial oxide. Dissolve in 10 c.c. of warm sodium hydroxide solution, add 20 c.c. of dilute hydrochloric acid, and make the solution up to 250 c.c. in a standard flask.

Measure 25 c.c. of the solution into a conical flask, add 10 c.c. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine solution, using starch as indicator (*cf.* p. 108).

Determination of Arsenic Oxide.—In strongly acid solution, arsenic acid is reduced by hydriodic acid to arsenious acid with liberation of iodine:



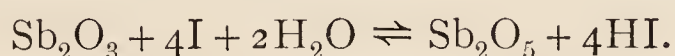
The reaction is complete within a few minutes if the solution is very strongly acid.

Evaporate 50 c.c. of the arsenic solution until the volume is reduced to about 5 c.c., cool, and pour into a 200 c.c. conical flask. Do not rinse the basin with water. Prepare a solution of hydriodic acid by dissolving 2 grams of potassium iodide in 10 c.c. of water and adding 10 c.c. of concentrated hydrochloric acid (free from chlorine). Rinse the basin into the flask with this solution.

Cover the flask with a watch-glass, and set aside for at least ten minutes. Then dilute to about 50 c.c., and titrate the liberated iodine with decinormal sodium thiosulphate *without* using starch indicator.

Antimony.

Antimonious oxide interacts with iodine in the same way as arsenious oxide, and antimony may be determined by titration with a standard iodine solution in a similar manner:



The hydriodic acid formed in the reaction must be neutralised by means of sodium bicarbonate as in the case of arsenic. In order to prevent precipitation of the antimony when an acid solution is diluted, or neutralised, tartaric acid is added.

Antimony in Tartar Emetic.—Weigh accurately about 4 grams of tartar emetic and dissolve it in about 100 c.c. of hot water. Cool the solution and dilute it to 250 c.c. in a standard flask. Measure 25 c.c. into a conical flask, add 10 c.c. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine. Run the iodine solution down the side of the flask in order to avoid loss of carbon dioxide (*cf.* p. 108), and use starch indicator as usual.

Antimony in Antimony Oxide.—Weigh accurately about 1.8 gram of antimony oxide. Dissolve the oxide by warming in a beaker with 5 c.c. of concentrated hydrochloric acid, and then add about 5 grams of tartaric acid dissolved in a little water. Transfer the solution and the rinsings of the beaker to a 250 c.c. standard flask, cool, and dilute to the graduation mark. Measure 25 c.c. of the solution into a conical flask, add 25 c.c. of a saturated solution of sodium

bicarbonate, and titrate with decinormal iodine as described under tartar emetic.

In case the sample contains antimonious oxide, reduce the antimonious to antimonious chloride in another portion of the solution by adding about 1 gram of sodium sulphite (or by passing sulphur dioxide through the warm solution). Boil the solution gently for five minutes and then pass a current of carbon dioxide through the boiling solution until the sulphur dioxide is expelled. Cool the solution, add 25 c.c. of sodium bicarbonate solution, and titrate with decinormal iodine.

Tin in an Alloy.

Preparation of a Solution for Analysis.—(1) Dissolve a weighed portion of the alloy (from 0.1 to 1 gram, according to the amount of tin) in concentrated hydrochloric acid with careful exclusion of air. This simple method is possible with some alloys such as solders and pewters and is described on p. 273.

(2) If the alloy is not completely soluble in hydrochloric acid alone, place it in a small flask on the steam-bath with 25 c.c. of the acid and add about 0.5 c.c. of bromine, or a few crystals of potassium chlorate from time to time. When completely dissolved, boil the solution to expel bromine or chlorine.

(3) Dissolve the weighed portion in 10 to 20 c.c. of concentrated sulphuric acid as described on p. 89 for type metal. When the disintegration is complete and all sulphur dioxide expelled, allow to cool and dilute to 100 c.c.

(4) If the alloy cannot be brought into solution by any of the above methods, disintegrate it with nitric acid as described on p. 272, dilute to about 30 c.c., filter, and wash the residue with hot water. Analyse the residue by the method given for an ore (p. 120), or for tin in bronze (p. 277).

Reduction and Titration.—The tin is reduced to the stannous condition by warming the solution containing hydrochloric acid with metallic iron or nickel, or by boiling it with metallic antimony. The stannous chloride is then determined by titration with standard iodine solution.

Stannous chloride is very readily oxidised by atmospheric

oxygen, and it is essential, therefore, that the solution should be protected from contact with the air both before and during the titration. This is accomplished by keeping the flask filled with carbon dioxide.

In strongly acid solution, neither arsenic nor antimony in the *trivalent* state interacts with iodine, and the presence of AsCl_3 or SbCl_3 does not interfere with the determination of tin by this method. If copper is present (more than 5 per cent.) it is best to remove it (together with arsenic and antimony) by precipitation with metallic iron as described below.

Procedure.—(a) If copper, arsenic, or antimony is present, place the solution, diluted to 100 c.c. and containing 25 per cent. by volume of concentrated hydrochloric acid, in a 300 c.c. beaker. Place a clean iron rod or a coil of piano wire in the solution, and keep near the boiling-point for about thirty minutes or until the solution becomes colourless. (Copper, arsenic, and antimony are precipitated, and tin is for the most part reduced to stannous chloride.) Remove and rinse the iron, filter the solution into a 400 c.c. flask, and proceed at once as described in (b).

(b) If copper, arsenic, and antimony are absent (or have been removed), place the solution in a 400 c.c. flask fitted with a rubber stopper carrying a bent inlet tube for carbon dioxide, and a straight, wide tube, about 3 ins. $\times \frac{5}{16}$ in. Add 50 c.c. of concentrated hydrochloric acid and about 1 gram of antimony powder (*free from sulphide*), and dilute to 200 c.c.

Pass a slow current of carbon dioxide through the flask, and boil briskly for fifteen minutes. Cool the solution by placing the flask in cold water, while passing a *rapid* current of carbon dioxide through the flask. When cold, add starch solution and titrate with decinormal iodine. Run in the iodine solution through the straight tube without lifting the rubber stopper, and maintain a current of carbon dioxide through the flask during the titration.

The end-point in the titration is attained when a blue coloration persists throughout the solution. The blue coloration may subsequently disappear on account of further reduction by the antimony, but this occurs so slowly, in the cold, that it does not interfere with the titration.

Tin in an Ore.

Preparation of a Solution for Analysis.—Fuse about 8 grams of potassium hydroxide in a spun iron crucible, and continue the heating until all moisture is expelled and quiet fusion attained. Cool, add about 0.5 gram (accurately weighed) of the finely powdered ore, cover the crucible, and heat, at first cautiously, and then with a full Bunsen flame until action ceases. Pour the molten mass into a clean nickel basin floating in a dish of water, and cover the hot mass with a crucible lid to prevent loss when the mass cracks during cooling.

Place the iron crucible in a porcelain basin, add 100 c.c. of water, and boil. If any of the fused mass remains attached to the crucible, add a little hydrochloric acid, and assist the solution process by breaking off any adhering lumps with a glass rod. When the crucible is clean, remove and rinse it. To the solution add the detached cake, together with the crucible lid if there is anything attached to it. Add 30 c.c. of concentrated hydrochloric acid and boil. There should be no undissolved residue from the ore, but there may be a few scales of ferric oxide from the crucible.

Transfer to a 400 c.c. conical flask, add 30 c.c. of concentrated hydrochloric acid, dilute to about 200 c.c. with hot water, and proceed at once with the reduction and titration as described on p. 119.

Standard Silver Nitrate and Potassium Thiocyanate

DECINORMAL SILVER NITRATE.

(N/10 solution contains 16.99 grams AgNO_3 per litre.)

STANDARD silver nitrate solution is used mainly for the determination of chloride, following either (1) Mohr's method of direct titration with potassium chromate as indicator, or (2) Fajans's method of direct titration with fluorescein as indicator, or (3) Volhard's method in which the silver nitrate is used in conjunction with a standard solution of potassium (or ammonium) thiocyanate, with a ferric salt as indicator. The first and second methods are applicable only if the chloride solution is neutral. Volhard's titration is done in an acid solution and is of wider application. The same standard solutions of silver nitrate and potassium thiocyanate may also be used for the determination of bromide, iodide, and cyanide; chlorate, bromate, and iodate; silver and mercury.

A solution made by dissolving 16.99 grams of pure silver nitrate in water and diluting to 1 litre is accurately decinormal. If ordinary commercial silver nitrate is used, an approximately decinormal solution is prepared (17 grams per litre) and is standardised with A.R. potassium (or sodium) chloride.

Standardisation of Silver Nitrate Solution.—If the silver nitrate is to be used in accordance with Volhard's method, it must be standardised by the method described on p. 128; if Mohr's or Fajans's method is to be followed, the solution is standardised as described below.

Dry the potassium chloride by heating it in a porcelain

basin or fuse it in a platinum basin and break up the fused mass. Weigh accurately about 1.85 gram of the salt, dissolve it in water, and dilute the solution to 250 c.c. in a standard flask. Titrate 25 c.c. of the solution with the silver nitrate, as described in the next paragraph.

Titration of a Chloride Solution by Mohr's Method.—This method, in which potassium chromate is used as an indicator, is based on the fact that silver chromate is much more soluble than silver chloride (25 mgrms. as compared with 1.5 mgrm. per litre at 18°). If silver chromate, which is bright red, is shaken with potassium chloride solution, it is immediately converted into silver chloride; and if silver nitrate solution is added to a solution of potassium chloride containing a little potassium chromate, all the chloride will be precipitated as silver chloride before any silver chromate (recognised by its red colour) is permanently formed, and the end-point of the chloride precipitation is thereby indicated. The chloride solution must be neutral or very faintly alkaline, because silver chromate is readily soluble in dilute acid. If the solution is acid, it is usually permissible to neutralise it by adding a slight excess of pure calcium carbonate.

Dilute 25 c.c. of the chloride solution to about 70 c.c. in a porcelain basin, and add 1 c.c. of a 2 per cent. solution of neutral potassium chromate¹ (free from chloride). Run the silver nitrate slowly into the chloride solution, with constant stirring. Silver chloride is precipitated, and a red precipitate of silver chromate also forms locally, but disappears on stirring. After all the chloride is precipitated, however, the addition of more silver nitrate produces a permanent precipitate of silver chromate. Continue the titration, therefore, until a *faint* reddish-brown tinge persists even after brisk stirring. Until some experience has been gained, it is a common mistake to add too much silver nitrate. After completing the first titration, it is advisable, therefore, to destroy the reddish-brown coloration by adding a few drops of ammonium chloride and to keep the mixture (protected from daylight until required) as a guide for a second titration

¹ The side-shelf reagent (0.2N) is suitable. If the solution contains chloride, add a few drops of silver nitrate, and filter. Make a 1 c.c. pipette (Fig. 27, p. 55) for measuring the potassium chromate solution,

made in another similar basin. The first tinge of a permanent reddish-brown coloration is more easily observed by comparison with this mixture.

Before the permanent colour change that marks the end-point of this titration can be recognised, a certain minimum amount of silver chromate must be permanently formed, and a measurable excess of silver nitrate is required to precipitate this minimum amount. The excess that is necessary depends on several factors, *e.g.* the solubility of silver chromate in the solution at the end-point, and the ability of the analyst to recognise slight colour changes. It is desirable to eliminate the personal factor as far as possible by making all determinations under the same conditions, *e.g.* amount of indicator, and volume of solution at the end-point. The unavoidable error amounts to, in general, at least 1 drop (about 0.05 c.c.) of silver nitrate, *i.e.* at least 0.2 per cent. if the titration requires about 25 c.c. of silver nitrate. No correction need be made, however, when standardising the silver nitrate solution if it can be arranged that approximately the same volume of silver nitrate (25 c.c.) will be required when determining the amount of chloride in a solution, since in that case the titration errors will not affect the final result.

Titration of a Chloride in Neutral Solution by Fajans's Method.—In this method the sodium salt of fluorescein plays the part of an indicator, but in a manner essentially different from that of potassium chromate in Mohr's process. If freshly precipitated silver chloride, after having been carefully washed, is suspended in a solution of sodium fluoresceinate, it retains its white appearance. If, now, a drop of silver nitrate solution is added to the suspension, the silver chloride at once becomes red in colour. The explanation of the colour change is as follows:—The fine particles of silver chloride readily adsorb silver ions (added as silver nitrate), become thereby positively charged, and can then adsorb the negatively charged fluorescein anions; this causes the particles to change colour on account of the formation of red silver fluoresceinate on their surface. It must be carefully observed that the adsorption of the fluorescein ion by silver chloride and the resulting colour change occur only when

an excess of silver ion is present in the solution surrounding the silver chloride.

If, therefore, silver nitrate solution is slowly added to a solution of potassium chloride containing fluorescein, no colour change is observed until the precipitation of the chloride is complete and a minute excess of silver nitrate has been introduced. At this point, which is sharply defined, the precipitated silver chloride becomes pale pink, and the colour change marks the end-point of a titration by Fajans's method. Substances like fluorescein, the action of which as indicators depends on the phenomenon of adsorption, have been described as "adsorption indicators." The indicator used for the titration of a chloride by this method is a 0.03 per cent. solution of the sodium salt of fluorescein,¹ and 1 c.c. of the solution is taken for every 25 c.c. of silver nitrate required. The chloride solution must be neutral or very faintly alkaline. The titration is carried out as follows:—

Measure 25 c.c. of the standard potassium chloride solution into a porcelain basin, add an equal volume of water and 1 c.c. of the indicator solution. Run the silver nitrate slowly into the chloride solution, with constant stirring. (The precipitated silver chloride remains colloidal at first but coagulates freely near—at about 1 c.c. short of—the end-point.) Continue the titration, meanwhile stirring continuously but not violently, until a permanent pink colour is suddenly observed in the turbid mixture.

It must be noted that the colour change occurs, not in the solution, but on the surface of the silver chloride particles. It is more easily seen while the mixture is being stirred. The end-point is sharply defined and the titration error is almost negligible—not more than 0.1 per cent. (Compare Mohr's method.) A sharper end-point is obtained if the titration is completed somewhat rapidly, so that part, at least, of the silver chloride remains colloidal at the end-point. If the precipitate is completely coagulated, the adsorbing surface is much reduced and the colour change is evident only on the surface of the flocculated precipitate and is not apparent in the mixture as a whole. If the concentration of

¹ This salt is sold as "soluble fluorescein."

the chloride solution is less than 0.01N, a sharp end-point is not obtained, and Fajans's method is therefore not applicable to very dilute solutions.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE.

Chloride, Bromide, and Iodide.

Mohr's Method.—The chlorides and bromides of sodium potassium, magnesium, and calcium, in neutral solution, may be determined by titration with standard silver nitrate, using potassium chromate as indicator. The procedure is described on p. 122. In the case of barium chloride it is necessary (since barium chromate is insoluble) to precipitate the barium by adding sufficient potassium sulphate. The precipitated barium sulphate does not interfere with the titration.

For iodides the method is unsatisfactory and should be avoided.

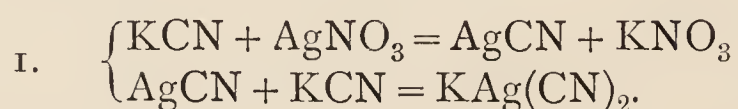
Fajans's Method.—The titration of the chlorides of sodium and potassium by this method, using fluorescein as an adsorption indicator, is described in the preceding section. In presence of divalent cations like calcium and magnesium, which cause immediate coagulation of the silver chloride precipitate, the titration is not quite so accurate.

The bromides of sodium and potassium may be determined by the same method, the colour change at the end-point being very sharp and more easily observed than with chlorides. A better indicator for bromide is the sodium salt of eosin. A 0.05 per cent. solution of "soluble eosin" is prepared, and 1 c.c. is used for every 25 c.c. of decinormal silver nitrate required in the titration. Coagulation of the silver bromide occurs within 0.1 c.c. of the end-point, and at the end-point the precipitate becomes brick-red. The colour change is much sharper than with fluorescein, and the titration error is negligible. With this indicator, bromide can be titrated in faintly acid solution (less than 0.1N acetic acid) with even greater precision than in neutral solution, and accurate results can be obtained with very dilute solutions (0.001N). Bromide cannot be titrated in presence of divalent cations with either fluorescein or eosin.

The iodides of sodium and potassium can be titrated in either neutral or faintly acid solution, using the eosin indicator.

Cyanide.

When silver nitrate is added to a solution of an alkali cyanide, it produces, locally, a precipitate of silver cyanide which, however, dissolves in the excess of the alkali cyanide and forms a soluble complex cyanide:



After all the cyanide has been converted into this complex salt, the addition of more silver nitrate produces a permanent precipitate of silver cyanide:



The cyanide in a solution may therefore be determined by titration with standard silver nitrate until a *permanent* precipitate is produced. This indicates that all the cyanide has been converted into the complex salt, and marks the beginning of reaction 2. The addition of a few drops of potassium iodide makes the end-point sharper. In presence of ammonium salts, silver cyanide is not precipitated, and potassium iodide *must* be added as an indicator.

Procedure.—Add excess of sodium hydroxide and a few drops of potassium iodide to the cyanide solution contained in a beaker, and dilute the mixture until the concentration of the cyanide solution is less than 0.02 normal. Place the beaker on a sheet of *black* paper, and run the standard silver nitrate slowly into the cyanide solution, with constant stirring, until the first permanent opalescence appears.

One molecule of silver nitrate corresponds to *two* molecules of potassium cyanide, *i.e.*, 1 c.c. of normal silver nitrate corresponds to 0.1302 gram of potassium cyanide.

Exercise.—Determine the percentage of potassium cyanide in a sample of commercial cyanide. Weigh accurately 3 to 3.5 grams, dissolve in water together with about 2 grams of sodium hydroxide, and make up to 250 c.c. in a standard flask. Use 25 c.c. of the solution for each titration. The commercial practice is to express the result as so much per

cent. of *potassium* cyanide. As commercial cyanide is often mainly *sodium* cyanide, many samples give a "percentage" considerably above 100.

DECINORMAL SILVER NITRATE AND DECINORMAL POTASSIUM THIOCYANATE.

When potassium thiocyanate is added to silver nitrate, a white precipitate of silver thiocyanate is produced. In order to mark the end-point, a ferric salt (free from chloride) is added to the silver solution. No ferric thiocyanate is permanently formed until all the silver is precipitated as thiocyanate, and the appearance of a permanent brownish coloration (ferric thiocyanate) shows when precipitation is complete. The titration must be performed in acid solution, and nitric acid is therefore added to the silver solution.

The thiocyanates of the alkalis are deliquescent salts, and a standard solution cannot be prepared by weighing a definite quantity. An approximately decinormal solution is therefore made by dissolving about 10 grams of potassium thiocyanate (or 8 grams of ammonium thiocyanate) in a litre. A solution of silver nitrate (approximately decinormal) is also required, and is made by dissolving 17 grams in 1 litre of water (see p. 121). These solutions are standardised as described below.

Preparation of the Indicator Solution.—Dissolve 5 grams of iron alum in 50 c.c. of water, add 50 c.c. of concentrated nitric acid (free from chloride), and boil the solution vigorously to expel oxides of nitrogen. Use 5 c.c. of the solution for each titration.

Titration of Silver Nitrate with Potassium Thiocyanate.—The thiocyanate solution must be run into the silver nitrate solution, not *vice versa*. Add 5 c.c. of the indicator solution to 25 c.c. of the silver nitrate contained in a porcelain basin, dilute to about 75 c.c., and then run in the thiocyanate slowly, with constant stirring. The first tinge of a permanent brown coloration marks the end-point. The brown coloration, which must persist after *brisk* stirring, is more easily seen if the precipitate is allowed to settle. After completing the first titration, destroy the brown

coloration by adding about 1 c.c. of silver nitrate, and keep this mixture as a guide for a second titration made in another similar basin (*cf.* p. 122).

After the silver nitrate solution has been standardised (as described in the next paragraph), the normality of the thiocyanate solution may be calculated.

Standardisation of the Silver Nitrate (*Volhard's Method*).—Weigh accurately 0.17 to 0.18 gram of pure, dry potassium chloride, or 0.13 to 0.14 gram of sodium chloride, and dissolve in 20 to 30 c.c. of water in a small stoppered bottle. Add about 1 c.c. of dilute nitric acid and 25 c.c. of the silver nitrate solution. Shake the bottle vigorously until the precipitate coagulates and leaves the supernatant liquid clear. Filter¹ through a small paper into a porcelain basin. Rinse the bottle and wash the precipitate with cold water until all the silver nitrate is removed. To the filtrate and washings add the ferric indicator, and titrate with thiocyanate.

Calculation.—It was found that 24.10 c.c. of a thiocyanate solution was required for 25 c.c. of a silver nitrate solution.

Of this silver nitrate, 25 c.c. was added to 0.1720 gram of potassium chloride, and the filtrate required 1.21 c.c. of the thiocyanate.

The excess of silver nitrate corresponds to 1.21 c.c. of the thiocyanate = $1.21 \times \frac{25.0}{24.1} = 1.25$ c.c. of the silver nitrate solution.

The volume of the silver nitrate solution corresponding to 0.1720 gram of potassium chloride is, therefore, $25 - 1.25 = 23.75$ c.c.

The silver nitrate is, therefore, $\frac{1000 \times 0.1720}{23.75 \times 74.6}$ normal,
= 0.0971 N.

¹ If the silver chloride is not removed by filtration, the end-point of the subsequent titration is indefinite and inaccurate, because silver chloride interacts with ferric thiocyanate and is converted into the *less soluble* silver thiocyanate. Pure potassium bromide (0.27 to 0.28 gram) may be used instead of potassium chloride for the standardisation and has the advantage that filtration is unnecessary, because silver bromide is less soluble than silver thiocyanate.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE AND STANDARD THIOCYANATE.

Chloride, Bromide, and Iodide.

Chloride.—The determination of a chloride is carried out in a manner exactly similar to the method of standardisation described above.

To the chloride solution, acidified with nitric acid, add a measured volume of standard silver nitrate in *slight* excess, and shake or stir the mixture vigorously until the silver chloride coagulates and settles. Filter the silver chloride, and wash it with cold water. (If care has been taken to use quite a *small* excess of silver nitrate, very little washing is required.) Titrate the excess of silver nitrate in the filtrate with thiocyanate.

Exercise.—Determine the concentration of the dilute hydrochloric acid on the bench. Dilute 10 c.c. to 250 c.c. in a standard flask, and titrate portions of 25 c.c. as described above.

Bromide.—In this case it is unnecessary to filter off the silver bromide before titrating the excess of silver nitrate, since the interaction of silver bromide with ferric thiocyanate is negligible. Otherwise the procedure is the same as for chloride.

Iodide.—When silver nitrate is added to an iodide solution, the precipitated silver iodide encloses a considerable amount of the soluble iodide or of the silver nitrate, and an error in the titration results. The procedure must therefore be modified as follows:—

To a measured volume of the iodide solution, contained in a stoppered bottle, add a little nitric acid, and dilute to about 250 c.c. Add standard silver nitrate gradually from a burette, 1 to 2 c.c. at a time, and after each addition insert the stopper and shake the bottle vigorously. Continue the addition of silver nitrate until a slight excess is present, when the precipitate coagulates and the supernatant liquid becomes clear. Then add 5 c.c. of the ferric indicator, and, without filtering, titrate the excess of silver nitrate with standard thiocyanate.

Chlorate.

The chlorate is reduced to chloride by gently boiling with a considerable excess of sulphurous acid solution, or by saturating the cold solution with sulphur dioxide and then boiling for about five minutes. The excess of sulphur dioxide is then expelled by passing a current of carbon dioxide through the boiling solution for about twenty minutes, and the chloride in the solution is determined in the usual manner with standard silver nitrate and thiocyanate.

If there is any chloride in the chlorate, a separate portion of the solution must be titrated without previous reduction, and the amount of chloride so found must be deducted from the titre representing the total chlorate plus chloride.

Exercise.—Determine the percentage of potassium chlorate in a sample of the commercial salt. Weigh accurately about 2.8 grams, dissolve in water, and dilute to 250 c.c. in a standard flask. Use 25 c.c. for each titration.

Silver.

Silver may be determined by titration of a solution with standard thiocyanate in the usual manner. With the exception of mercury, the presence of other metals does not, as a rule, interfere with the titration.

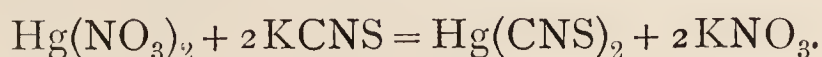
Exercise.—Determine the percentage of silver in a silver coin. Clean a threepenny piece with emery cloth and weigh it accurately. Place it in a 200 c.c. conical flask, add 5 c.c. of water and 10 c.c. of concentrated nitric acid, and warm gently until the coin is dissolved. Add a little water, and boil for five minutes in order to expel oxides of nitrogen. Dilute the cold solution to 100 c.c. in a standard flask, and use 25 c.c. for each titration.

Mercury.

Mercury may be determined in the same manner as silver by titration with standard thiocyanate. The solution must contain a large excess of nitric acid, and the mercury must be present as mercuric nitrate. The original substance should therefore be dissolved in hot, concentrated nitric acid, and, after making up to a definite volume, a portion

of the solution should be tested for mercurous nitrate by adding hydrochloric acid.

The reaction that occurs in the titration is as follows:—



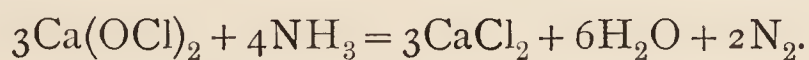
As mercuric thiocyanate is somewhat soluble in water, it may not be precipitated; but this does not interfere with the titration, and no ferric thiocyanate is permanently formed until the above reaction is complete.

Exercise. — Determine the percentage of mercury in mercuric oxide. Weigh accurately about 1 gram of mercuric oxide. Dissolve in concentrated nitric acid and dilute the solution to 100 c.c. in a standard flask. To 25 c.c. of the solution, add 10 c.c. of concentrated nitric acid and 5 c.c. of the ferric indicator, dilute to about 70 c.c., and titrate with standard thiocyanate.

Total Chlorine in Bleaching Powder.

Besides “available” chlorine, bleaching powder may contain chlorine as chloride and chlorate which is useless for bleaching purposes (see p. 115). In order to determine the total chlorine, prepare a solution of the bleaching powder in the manner described on p. 115, and proceed as follows:—

Hypochlorite and Chloride. — Measure 25 c.c. of the solution into a beaker, add 10 c.c. of dilute ammonia, cover the beaker, and boil gently for about five minutes. The hypochlorite is thus converted into chloride, and nitrogen is liberated:



Add excess of dilute nitric acid, carefully avoiding loss through effervescence, and boil until free from carbon dioxide. Add excess of decinormal silver nitrate (25 to 30 c.c.), stir until the precipitate coagulates, filter, and wash. Titrate the excess of silver nitrate in the filtrate with standard thiocyanate in the usual way.

Hypochlorite, Chloride, and Chlorate. — Boil 25 c.c. of the solution with dilute ammonia as before. Cool the solution and saturate with sulphur dioxide in order to reduce any chlorate to chloride. Boil for five minutes. Acidify with dilute sulphuric acid and expel the excess of

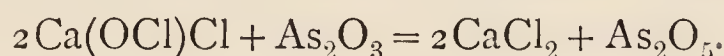
sulphur dioxide by passing carbon dioxide through the boiling solution. (The last trace of sulphur dioxide may be destroyed by carefully adding dilute potassium permanganate until the solution is faintly pink.) All the chlorine in the bleaching powder is now present in the solution as chloride, which may be determined by means of standard silver nitrate and thiocyanate in the usual manner.

The percentage of total chlorine in the bleaching powder may then be calculated, and also (by difference) the percentage of chlorine present as chlorate. If the available chlorine in the same sample has been determined (pp. 115 and 133), the amount of chlorine (not available) present as chloride may also be calculated.

Various Volumetric Processes

Available Chlorine in Bleaching Powder by means of Standard Sodium Arsenite.

THIS method depends on the oxidation of sodium arsenite to sodium arsenate by the hypochlorite. The reaction may be represented by the following (simplified) equation:—



Standard sodium arsenite solution (p. 108) is run into the bleaching powder solution from a burette, and the end of the reaction is determined by means of potassium iodide-starch paper; so long as any hypochlorite remains undecomposed, a blue stain is produced on the test-paper when a drop of the solution is brought into contact with it. The procedure is as follows:—

Prepare a solution of the bleaching powder in the manner described on p. 115. After shaking, measure 25 c.c. of the turbid mixture into a small beaker and make a rough titration by running in the standard sodium arsenite, rapidly at first, and then 0.5 c.c. at a time, stirring constantly, until a drop of the solution gives no blue stain when placed on potassium iodide-starch paper.

Repeat the titration, only on this occasion remove no test drops until within about 1 c.c. of the previously determined end-point. As the end-point is approached, the blue stain becomes less pronounced, and is last seen near the centre of the wet spot on the test-paper. The end-point is quite sharp.

Calculate the percentage of available chlorine in the bleaching powder.

Preparation of Potassium Iodide-Starch Paper.—Grind 0.5 gram of starch with a little cold water, pour into 100 c.c. of boiling water, boil for a minute, and cool. Add about 2 c.c.

of 10 per cent. potassium iodide solution. Dip strips of filter paper into the mixture and hang them over a glass rod until dry. Preserve the strips in a stoppered bottle.

Iron by Means of Standard Titanous Chloride.

Titanous chloride is a powerful reducing agent which may be used to determine a variety of substances, organic as well

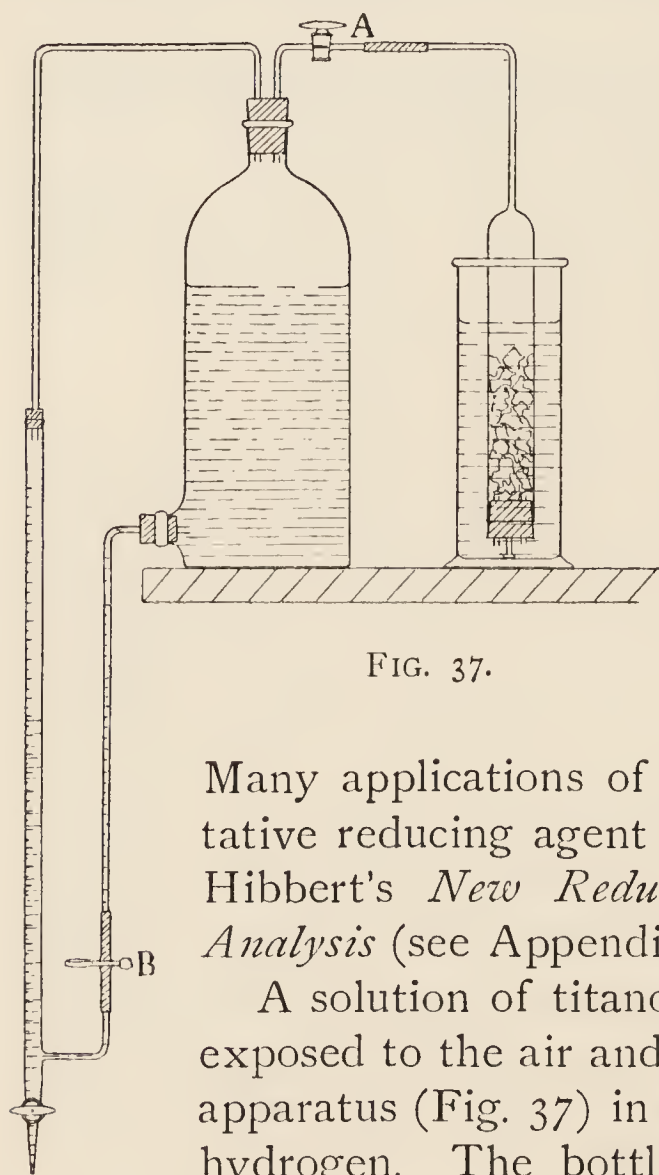


FIG. 37.

as inorganic, by volumetric methods. In presence of acid it reduces ferric salts to ferrous salts, chromates to chromic salts, and chlorates to chlorides; in alkaline solution nitrates are reduced to ammonia. Organic nitro-compounds, such as nitrobenzene and picric acid, are reduced to the corresponding amines; azo-compounds and dyestuffs like indigo are reduced and decolorised.

Many applications of titanous chloride as a quantitative reducing agent will be found in Knecht and Hibbert's *New Reduction Methods in Volumetric Analysis* (see Appendix, p. 429).

A solution of titanous chloride oxidises rapidly if exposed to the air and it must be kept in a suitable apparatus (Fig. 37) in which the air is replaced by hydrogen. The bottle (2 litres) is connected permanently with a burette and with a hydrogen generator. The latter consists of a cylinder containing hydrochloric acid (1 : 2), and an inner tube which is half-filled with granulated zinc. The inner tube is closed at the lower end with a cork pierced with two holes to admit the acid and with a third hole for a short piece of glass rod that serves to keep the cork off the bottom of the cylinder.

The titanous chloride solution is prepared as follows:— In a small flask mix 75 c.c. of commercial titanous chloride (15 to 20 per cent. solution) with 100 c.c. of concentrated hydrochloric acid and boil the mixture for about a minute

to expel traces of hydrogen sulphide. Cool under the tap, dilute the solution to 2 litres in the storage bottle, and mix thoroughly. Connect the bottle with the burette and the hydrogen generator, and open the tap A. Open the clip B and allow a little of the solution to flow into the burette, then close B and open the burette tap. Allow hydrogen to escape from the burette for a few minutes in order to displace the air. Then close the burette tap and fill the burette with the solution through the clip B. The solution is then ready for use. (The tap A remains permanently open.)

Standardisation of the Solution. — The solution is standardised by titration against a known amount of a ferric salt in acid solution, using a large excess of ammonium thiocyanate as indicator.

Dissolve 12 grams of iron alum (weighed to the nearest centigram) in about 200 c.c. of dilute sulphuric acid and dilute the solution to 1 litre in a standard flask. Measure 25 c.c. of this solution into a conical flask, add 20 c.c. of a 20 per cent. solution of ammonium thiocyanate, dilute to 80 c.c., and titrate at once with the titanous chloride until the red coloration disappears. (Ferric thiocyanate solution decomposes slowly—the ferric ion being reduced to ferrous—and an error will result if the titration is unduly delayed.) Calculate the weight of iron equivalent to 1 c.c. of the titanous chloride solution.

The solution oxidises slowly in spite of precautions to exclude air, and it must be standardised at frequent intervals (usually every day). The iron alum solution is convenient for this purpose since it keeps indefinitely. If there is doubt about the purity of the iron alum, the concentration of the solution may be determined by titration with a titanous chloride solution that has been standardised on the same day with ferrous ammonium sulphate, as follows:—Weigh accurately about 3.5 grams of the salt, wash it into a 250 c.c. standard flask containing about 100 c.c. of dilute sulphuric acid, and dilute the solution to the mark. Oxidise 25 c.c. of the solution by running into it, from a burette, a dilute solution of potassium permanganate (about 0.02N) until a very faint pink coloration is obtained. Then add ammonium thiocyanate and titrate with the titanous chloride as already described.

Determination of Iron.—The solution must contain sulphuric or hydrochloric acid. If the iron is present entirely in the ferric condition, dilute the solution (or a measured portion of it) to about 60 c.c., add 20 c.c. of ammonium thiocyanate solution, and titrate with standard titanous chloride as described above.

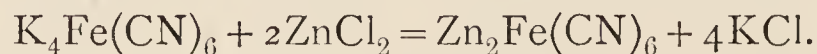
If any ferrous salt is present, this must first be oxidised. Provided the solution contains no hydrochloric acid, potassium permanganate is the most convenient oxidising agent (see above); in presence of hydrochloric acid the oxidation is effected by adding ammonia until alkaline and then hydrogen peroxide, and boiling for ten minutes. After dissolving the precipitated ferric hydroxide in excess of hydrochloric acid, the solution is ready for titration. It is obvious that titration with titanous chloride before and after oxidation will give the data required for calculating the respective amounts of ferrous and ferric salt in a solution containing both.

The iron in limestones and dolomites (p. 281), silicates (p. 285), glasses (p. 292), and in some alloys such as brass (p. 274), may be determined (after separation as ferric hydroxide) by this method.

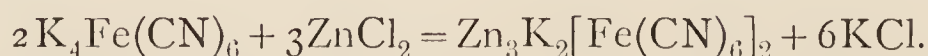
Exercise.—Determine the percentage of iron in iron wire. Weigh accurately from 0.15 to 0.2 gram of the wire and dissolve it in a mixture of 20 c.c. of water and 5 c.c. of concentrated sulphuric acid. Cool the solution and oxidise the ferrous sulphate by adding dilute potassium permanganate in the smallest possible excess. Dilute the solution to 100 c.c. in a standard flask. Use 25 c.c. for each titration.

Zinc by means of Standard Potassium Ferrocyanide.

When potassium ferrocyanide is added to an acid solution of a zinc salt, zinc ferrocyanide is first precipitated:—



The addition of more potassium ferrocyanide converts the zinc ferrocyanide into the zinc potassium salt, and the complete reaction may be represented by the following equation:—



The completion of the reaction may be determined by

means of an external indicator—a solution of uranium nitrate. The zinc solution, containing hydrochloric acid, must be heated to about 80° , and the potassium ferrocyanide solution added from a burette until a drop of the mixture is found to give a brown coloration (due to a slight excess of potassium ferrocyanide) when brought into contact with a drop of the indicator on a white porcelain plate.

The standardisation of the potassium ferrocyanide solution and the actual determination of the zinc must be carried out under as nearly as possible the same conditions. Oxidising substances, such as nitric acid, and other metals that give insoluble ferrocyanides, *e.g.* copper, cadmium, iron, lead, must be absent. Small amounts of lead or aluminium do not interfere.

The following solutions are required:—

Potassium Ferrocyanide Solution.—Dissolve 43 grams of potassium ferrocyanide— $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ —in water and dilute the solution to 1 litre. One c.c. corresponds to about 0.01 gram of zinc.

Standard Zinc Chloride Solution.—Ignite some pure zinc oxide in a porcelain crucible and cool in a desiccator. Weigh accurately about 3.1 grams. Dissolve in 10 c.c. of concentrated hydrochloric acid mixed with an equal volume of water, and dilute the solution to 250 c.c. in a standard flask.

Indicator Solution.—Dissolve 5 grams of uranium nitrate in 100 c.c. of water.

Standardisation of the Potassium Ferrocyanide Solution.—Measure 25 c.c. of the standard zinc chloride solution into a 400 c.c. beaker, add 10 c.c. of concentrated hydrochloric acid, a few drops of litmus as indicator, and neutralise the solution with ammonia. (The ammonium chloride thus formed makes the end-point sharper.) Add 3 c.c. of concentrated hydrochloric acid, dilute to 200 c.c., and warm to about 80° .

Run the ferrocyanide slowly into the zinc chloride solution, stirring briskly, until 24 c.c. has been added. The bluish-white precipitate becomes flocculent at about this stage. Add more ferrocyanide, drop by drop, until the precipitate becomes pale cream-coloured and loses its flocculent appearance. (This change always occurs within

less than 1 c.c. of the end-point of the titration and is a useful guide.) Now add the ferrocyanide drop by drop, stir briskly, and test the mixture by bringing 2 drops into contact with a drop of the indicator on a white porcelain plate. Stir very thoroughly after each addition of the ferrocyanide before testing with the indicator, and make a note of the burette-reading after each test. When a distinct brown coloration is obtained, wait for two or three minutes and it will be found that a coloration has developed in one or more of the preceding test-drops. The burette-reading corresponding to the first test-drop in which a coloration develops is taken as the end-point of the titration.

A correction must be made for the amount of ferrocyanide that must be added (after precipitation is complete) in order to give a coloration with the indicator. The correction is found in the following way:—Mix 10 c.c. of concentrated hydrochloric acid with about 50 c.c. of water, add a few drops of litmus, and neutralise the solution with ammonia. Add 3 c.c. of concentrated hydrochloric acid, dilute to 200 c.c., and warm to about 80° . Add the ferrocyanide drop by drop, and test the solution after the addition of each drop, until a brown coloration is observed. (Allow about two minutes for the coloration to develop.) This volume of ferrocyanide must be deducted from the burette-reading in the actual titration. It amounts, as a rule, to about 0.2 c.c.

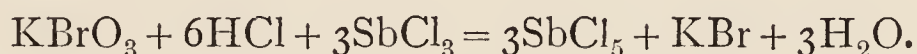
Procedure when the Quantity of Zinc is unknown.—The following method of titrating a solution containing an unknown quantity of zinc is convenient. After diluting the solution to 200 c.c. and warming to 80° , transfer one-half of the solution to another similar beaker. Add the ferrocyanide slowly to one portion of the solution, while stirring briskly, until the bluish-white precipitate becomes pale cream-coloured, and a brown coloration is obtained with the indicator. If, for example, no coloration was observed after adding 11 c.c., and a distinct coloration was obtained after adding 12 c.c., it is probable that at least 22 c.c. will be required for the whole solution. Mix the two portions of the solution, run in more ferrocyanide until 22 c.c. in all has been added, and stir vigorously. Pour the mixture into the second beaker (which still contains a trace of the original

solution), pour it back again into the first beaker, and finish the titration as usual.

Exercise.—Determine the percentage of zinc in a sample of commercial zinc oxide (zinc white). Weigh accurately about 3 grams of the oxide. Dissolve in 10 c.c. of concentrated hydrochloric acid, dilute the solution to 250 c.c. in a standard flask, and titrate 25 c.c. containing the same amounts of ammonium chloride and hydrochloric acid as indicated above.

Antimony by means of Standard Potassium Bromate.

When potassium bromate is added to a hot, acid solution of antimonious chloride, the latter is oxidised to antimonic chloride :



After complete oxidation of the antimony, any further addition of bromate results in the liberation of bromic acid and, ultimately, of bromine. Methyl orange may be used to show when the reaction is complete, since a mere trace of bromic acid (or bromine) is sufficient to destroy the colour of that indicator.

Arsenious chloride is also oxidised by potassium bromate, and arsenic may be determined in the same manner as antimony. If antimony is to be determined in presence of arsenic, the latter must be got rid of as indicated below. Neither tin, lead, silver, zinc, copper (less than 5 per cent.), nor iron (less than 10 per cent.) interferes with the determination.

Decinormal Potassium Bromate Solution.—Weigh accurately 2.784 grams of pure potassium bromate, dissolve in water and dilute the solution to 1 litre in a standard flask. If the potassium bromate is not pure (bromide is a common impurity), the solution must be standardised in one of the following ways:—

- (1) Weigh accurately about 1.2 gram of pure arsenious oxide. Dissolve in 10 c.c. of warm sodium hydroxide solution (*cf.* p. 108), transfer the solution to a 250 c.c. standard flask, add 5 c.c. of concentrated hydrochloric acid, and dilute to the graduation mark. To 25 c.c.

of the solution add 25 c.c. of water and 20 c.c. of concentrated hydrochloric acid. Titrate with the potassium bromate solution as described later.

- (2) Weigh accurately about 0.15 gram of pure, finely divided antimony, and transfer to a 250 c.c. conical flask. Add 20 c.c. of concentrated hydrochloric acid and a few drops of bromine. Warm *very gently* until the antimony is dissolved, and then boil the solution until the excess of bromine is expelled. Reduce the antimonious to antimonious chloride and titrate with the potassium bromate solution as described below.

Procedure.—Place the weighed sample of the ore or alloy (corresponding to not more than 0.15 gram of antimony) in a 250 c.c. conical flask, add 25 c.c. of concentrated hydrochloric acid and about 0.5 c.c. of bromine, and warm very gently until dissolved. Boil the solution to expel the excess of bromine.

Reduction of the Antimonious Chloride.—To the solution add 3 to 4 grams of sodium sulphite, rinse down the side of the flask with a little warm water, and boil the solution until the volume is reduced to rather less than 10 c.c. Any arsenic that may be present is reduced and volatilised together with the excess of sulphur dioxide. If the sample is known to contain more than 2 per cent. of arsenic, add 20 c.c. of concentrated hydrochloric acid and 5 c.c. of sulphurous acid solution, and boil down again. Then add 20 c.c. of concentrated hydrochloric acid and 40 c.c. of water.

Titration with Potassium Bromate.—Heat the solution until almost boiling. Run in the potassium bromate slowly (about 20 c.c. per minute), with continuous brisk stirring, until most of the antimony is oxidised. Then add 2 c.c. of methyl orange and continue the titration until the colour of the indicator disappears. The end-point is sharply defined.

If the methyl orange is added at the commencement of the titration, its colour gradually fades before the end-point is reached, and more indicator must then be added. A preliminary titration may be carried out in this way.

Exercise.—Determine the percentage of antimony in a sample of type metal (alloy of lead, antimony, and tin). Use about 0.5 gram.

PART III

GRAVIMETRIC ANALYSIS

IN the gravimetric method of analysis, the determination of weight is the principal quantitative measurement involved. Although, as a general rule, the procedure is less simple and the manipulation more difficult than in volumetric analysis, this is not necessarily the case. In order to determine, for example, the amount of zinc in a sample of basic zinc carbonate, a weighed quantity of the substance is heated in a crucible to dull redness until it is converted into zinc oxide. The weight of the zinc oxide is then ascertained, and, as the composition of the oxide is known, the percentage of zinc in the basic carbonate is easily calculated from the weight of the oxide obtained. It is obvious, however, that the result will not be correct unless the residue consists of zinc oxide only.

When a complete analysis of a complex substance is required, the analytical process is less simple, and it has already been stated that, as a rule, the constituents of the substance must be separated from one another before the amount of each can be ascertained. The separation is usually accomplished by precipitating each constituent in the form of an "insoluble" compound, which is then filtered, washed, dried, and weighed. The attainable accuracy of the analysis depends mainly on the insolubility of the precipitate, on the completeness of its separation from the other substances present, and on its composition at the time of weighing being perfectly definite and known.

One of the most difficult problems met with in quantitative analysis is the selection of good methods of separation. A perfect separation is rarely obtained by the methods adopted in qualitative analysis; these methods are often quite unsuit-

able, or require modification, for the purposes of quantitative analysis. The separation of iron and magnesium, for example, by means of ammonium chloride and ammonia, is imperfect. All the iron is precipitated as ferric hydroxide, but, even in presence of a large excess of ammonium chloride, the precipitate always contains more or less magnesium hydroxide. In order to separate the co-precipitated magnesium, the ferric hydroxide, after it has been filtered and washed, is dissolved in acid, and ammonium chloride and ammonia are again added to the solution. After filtering the ferric hydroxide, it may be necessary to dissolve it again and to precipitate it a third time before the separation of the iron and magnesium is complete. The several filtrates are then combined and the magnesium in solution is precipitated as magnesium ammonium phosphate.

It is evident, from the foregoing, that precipitation and filtration form an important part of the routine of gravimetric analysis. The general description of these operations is given in Part I., pp. 25-30, whilst some of the apparatus and processes peculiar to gravimetric analysis are described in the following pages.

NOTES ON APPARATUS.

(*See also p. 14.*)

Porcelain Crucibles. — For most ordinary purposes, crucibles of good porcelain, $1\frac{1}{4}$ to $1\frac{1}{2}$ inches in diameter, are suitable. Before being exposed to a high temperature, porcelain crucibles should be carefully heated with a small flame in order to avoid fracture. Porcelain crucibles must not be used for substances that are to be treated with hydrofluoric acid, or for fusions with sodium hydroxide, sodium peroxide, or alkali carbonates; and they are not so suitable as platinum crucibles for substances that require heating to a very high temperature. Porcelain crucibles may be permanently marked, for the purpose of identification, by writing in ink a distinctive letter on each crucible and lid, drying the ink by gently warming, applying more ink, and finally heating the porcelain to bright redness so as to burn the residual ferric oxide into the glaze.

Silica Crucibles.—Although probably more fragile than porcelain crucibles, silica crucibles may be safely exposed to sudden changes of temperature without any risk of fracture. Silica vessels must not be used for alkalis or hydrofluoric acid.

Platinum Crucibles.—When the use of a platinum crucible is admissible, it is usually preferable to one of porcelain. Platinum crucibles can be more readily and more uniformly heated to redness than porcelain crucibles. On account of the expense of platinum, however, it is often necessary to restrict the use of platinum vessels to cases where they are indispensable. *The following rules and precautions with regard to platinum vessels must be observed:—*

1. Platinum crucibles must not be exposed to the reducing area of a flame, or to a luminous flame, since this will cause the metal to lose its lustre and to become brittle—owing, probably, to the formation of a carbide of platinum.

2. Compounds of lead, silver, zinc, tin, bismuth, arsenic, and antimony must not be heated in platinum crucibles, since reduction to the metallic state may occur, and the metals, having comparatively low melting points, may alloy with the platinum.

3. Great care should be taken in igniting phosphates in platinum crucibles, since the presence of reducing substances, such as charred filter paper, may result in the formation of traces of phosphorus which, combining with the platinum, renders it brittle. It is safer to use a porcelain crucible for phosphates.

4. Platinum crucibles must not be used for fusions with hydroxides or nitrates of the alkalis.

5. Evaporations or fusions in which chlorine, bromine, or iodine is set free must not be performed in platinum vessels. This rule applies to mixtures in which both chloride and nitrate are present.

6. Care must be taken to avoid damaging a platinum crucible and causing indentations by dropping it on the bench. It must on no account be squeezed with the object of loosening the solidified cake after a sodium carbonate fusion.

7. Platinum ware should be kept scrupulously clean. Adhering substances or stains can sometimes be removed

by boiling a little concentrated hydrochloric acid in the crucible, or by fusing a little potassium bisulphate in the crucible and removing the salt by means of boiling water. The crucible should then be polished with fine, moist sea sand, which is gently rubbed on the surface of the metal with the finger. After polishing, the platinum should be rinsed with distilled water and dried.

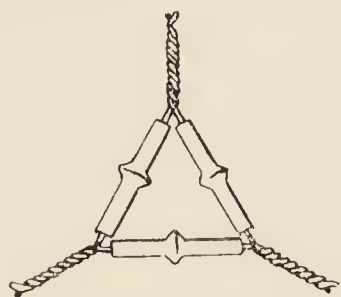


FIG. 38.

Palau Crucibles.—"Palau" is an alloy composed of 80 per cent. of gold and 20 per cent. of palladium. It is a useful substitute for platinum, being less costly, and palau crucibles are specially suitable for sodium carbonate fusions in silicate analysis, because the cold cake separates from the crucible much more readily and completely than from a platinum crucible. The alloy melts, however, at a lower temperature (1370°) than platinum (1750°), and a palau crucible must not be heated with a blow-pipe flame or (when empty) with a very powerful Méker burner. Palau crucibles should not be used for fusions with potassium pyrosulphate.

Triangles.—A very satisfactory form of pipe-clay or porcelain triangle, on which a crucible is placed during the process of heating, is shown in Fig. 38. For the usual sizes of crucibles, triangles with sides 2 inches and $2\frac{1}{2}$ inches long are suitable. Nickel wire is preferable to iron wire on account of its much greater durability.

Perforated Silica Plates.—It is often important to exclude flame gases from the interior of a crucible during an ignition, and, for this purpose, the device shown in Fig. 39 may be used. It consists of a silica plate, 5 inches square, in which is cut a round opening large enough to admit the crucible to two-thirds of its depth. The plate is held in an inclined position by means of a clamp. A higher temperature in the crucible may be reached by using a silica plate with a larger opening, and placing over the

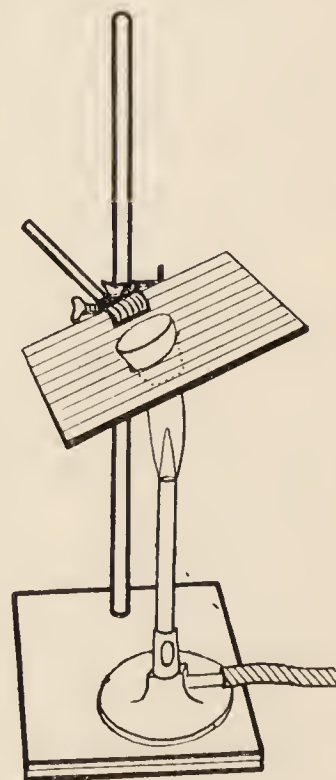


FIG. 39.

latter a disc of platinum in which a hole is cut to fit the crucible.

Crucible Tongs.—Crucible tongs should be made of brass or of gun-metal, and it is an advantage to have them fitted with platinum tips. They must be kept scrupulously clean.

The Gooch Crucible.

Filtration by means of a Gooch crucible is frequently advantageous, and is a most convenient method of collecting a precipitate directly in the crucible in which it is finally weighed. A porcelain Gooch crucible of the size and shape

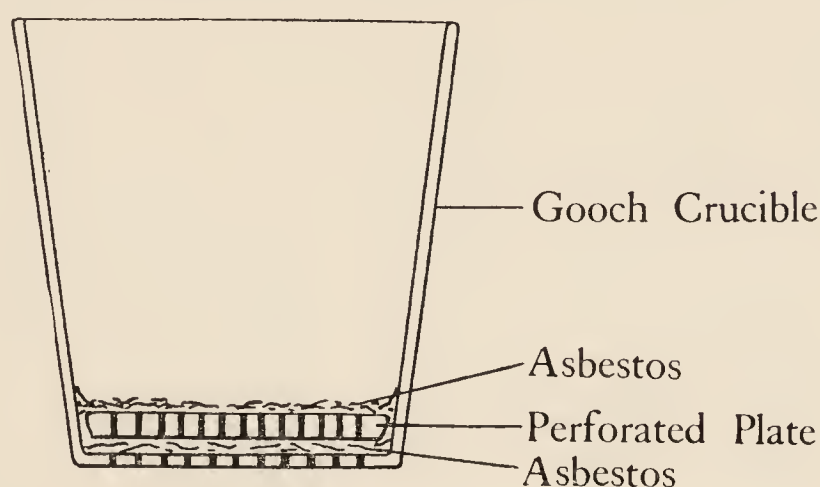


FIG. 40.—Section of Gooch Crucible (Actual Size).

shown in Fig. 40 is suitable for most purposes. The bottom of the crucible is perforated with a number of small holes. A useful accessory is a perforated porcelain disc equal in size to the crucible bottom. The crucible, which is always used in conjunction with the filter-pump, is fitted into a glass adapter by means of a narrow rubber ring (cut from a piece of rubber tubing, 1 inch in diameter), and the adapter passes through the rubber stopper of a filter-flask.

The filtering medium is fine, white, anhydrous asbestos, and a special quality is sold for the purpose. Suitable asbestos may be prepared from the fibrous amphibole variety—not from fibrous serpentine (chrysotile), which is hydrous. The asbestos is cut into pieces about $\frac{1}{4}$ inch long, any hard lumps being rejected, and is warmed on the steam-bath for an hour with hydrochloric acid (1 : 1) in order to extract soluble matter. It is then filtered (using a Büchner funnel, Fig. 4, p. 17) and thoroughly washed with water until free

from acid. The asbestos is then dried in the steam-oven and bottled.

Preparation of the Asbestos Filter.—Connect the filter-flask, fitted with the adapter supporting the crucible, to the filter-pump (Fig. 41). In using a Gooch crucible, it is most important that the filtration should not be conducted under too great a pressure, and, to prevent this, the connection with the pump should include some means of regulating the pressure, such as that described on the next page.

Shake about 0.03 to 0.05 gram of the asbestos with 25 c.c. of water and pour about 20 c.c. of the mixture into the

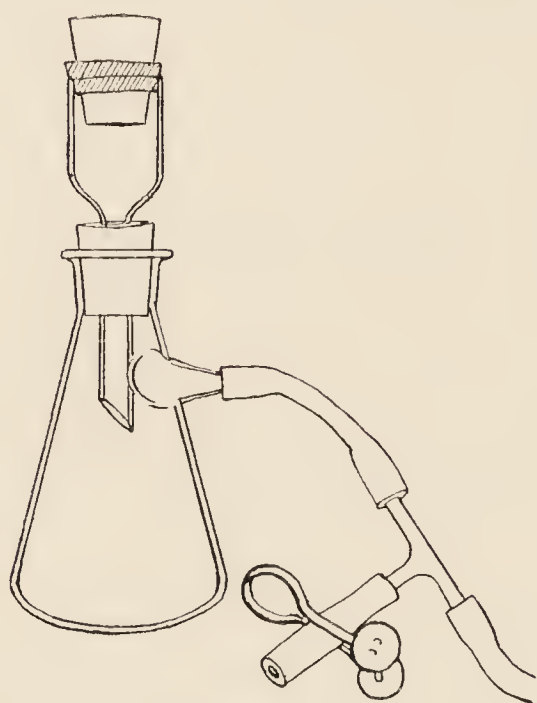


FIG. 41.

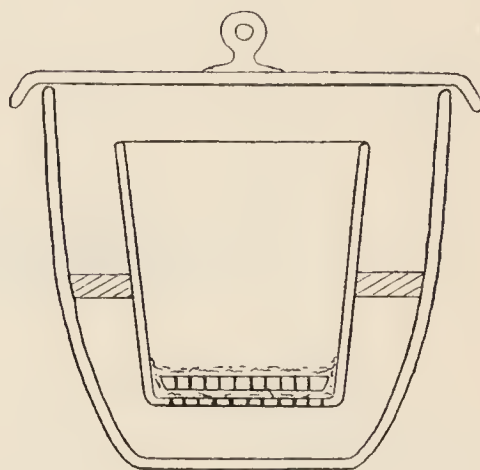


FIG. 42.

crucible. Allow the water to drain, using very gentle suction. Then turn on the maximum pressure the regulator will allow, and carefully drop the perforated disc into the crucible. Add the remainder of the asbestos and wash the filter with about 100 c.c. of warm water.

If the filter is properly prepared with suitable asbestos, 100 c.c. of water will pass through in about one minute under a pressure equal to that of 2 inches of mercury. Place the crucible on a watch-glass and dry it for an hour (in the steam-oven or air-oven) at the same temperature as that required for the precipitate that is subsequently to be collected in the crucible. If the precipitate requires ignition, place the crucible within a larger platinum crucible (or a nickel crucible, fitted with an asbestos ring, as shown in Fig. 42),

and heat the larger crucible with the flame. Cool the Gooch crucible in a desiccator, and weigh it. It is then ready for use.

Pressure Regulator for Use with the Filter-pump.—Some means should always be used of limiting the maximum pressure under which filtration by means of the filter-pump is conducted, and the following arrangement is simple and effective.

Three tubes pass through a rubber stopper fitted into a bottle (Fig. 43). A and B are connected to the filter-pump and to the filter-flask, respectively. The tube C is drawn out to form a capillary at its lower end and forms an air-leak. The size (or length) of the capillary is adjusted by trial, so that, when the pump is working at full power, the pressure in the bottle when B is closed cannot fall below a definite value, viz., about 2 inches of mercury less than atmospheric pressure. The adjustment is easily made with the help of a simple pressure gauge; a piece of glass tubing bent into a U-form and containing mercury is suitable for the purpose.

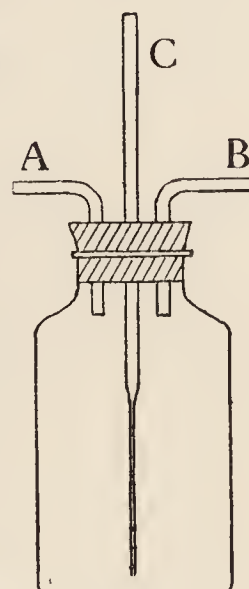


FIG. 43.

The bottle also safeguards the contents of the filter-flask from contamination with water from the filter-pump, should the water-pressure momentarily fail.

The Rose Crucible.

When it is necessary to ignite a precipitate in an atmosphere of hydrogen, carbon dioxide, or oxygen, a Rose crucible is used. The crucible, its cover, and the tube through which the gas is led into the crucible (all of porcelain or silica) are shown in Fig. 44.

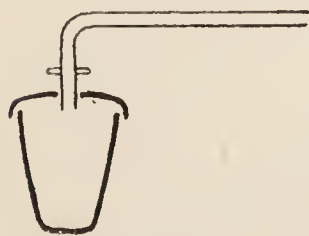


FIG. 44.

The crucible and lid should always be weighed separately because the lid sometimes breaks during the ignition.

Hydrogen should be prepared in a small Kipp generator from sulphuric acid (6N) and arsenic-free zinc. A little copper sulphate solution should be poured over the zinc before the generator is charged with acid. The gas must

be purified and dried by passing it through two wash-bottles—the first containing potassium permanganate solution acidified with dilute sulphuric acid, and the second containing concentrated sulphuric acid. Before the hydrogen is used, it must be tested and proved free from air by collecting a sample of the gas in a test-tube by displacement of air, and noting whether it burns quietly when ignited.

Carbon dioxide, prepared in a Kipp generator from marble and hydrochloric acid, must be washed and dried by passing it through a mixture of water and sodium bicarbonate and then through concentrated sulphuric acid.

Oxygen, supplied from a gas-holder (filled from a cylinder of the compressed gas), should be dried by passing it through concentrated sulphuric acid.

In all cases, the flow of gas is best regulated by means of a tap or a screw-clip placed on the rubber connection between the sulphuric acid wash-bottle and the crucible.

THE IGNITION AND WEIGHING OF PRECIPITATES.

After a precipitate has been filtered and washed, it requires further treatment before it can be weighed. In the first place, if a filter paper has been used it must be destroyed by incinerating it either in presence of the whole precipitate or after separating the precipitate from it. The precipitate, together with the filter ash, is then “ignited” in a weighed crucible. (The terms “ignite” and “ignition” are commonly used in analytical chemistry, and refer to the process of heating a substance to a high temperature, without allowing the direct access of the flame to the substance.) The purpose of the ignition is (1) to dry or dehydrate the precipitate completely, and, in many cases, (2) to convert the precipitate, which may be of uncertain composition, into another compound of definite and known composition. Copper, for example, may be precipitated as hydrated copper oxide, $\text{CuO} \cdot x\text{H}_2\text{O}$, which is ignited and weighed as anhydrous cupric oxide, CuO ; and zinc may be precipitated as basic carbonate which is of variable composition but is easily converted by ignition into zinc oxide, ZnO . The weight of the ignited precipitate is then ascertained by weighing the crucible and its contents, and deducting the

weight of the crucible and that of the filter ash (unless the latter is negligible) from the total weight.

The ignition is performed by heating the crucible containing the precipitate with the flame of a Bunsen burner, a Méker burner, or a blowpipe, according to the temperature required.

The Bunsen Burner.—A good Bunsen burner, giving a flame of medium size, should be used for heating purposes. In order that it may be possible to obtain suitable non-luminous flames of different sizes, it is most important that the air-regulator of the burner should be in working order; it seldom happens that the mere lighting of the burner, without carefully adjusting the air supply, gives the best flame for a given purpose.

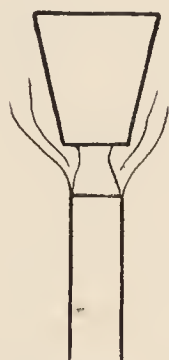


FIG. 45.

Incorrect Position
of Crucible in
Bunsen flame.

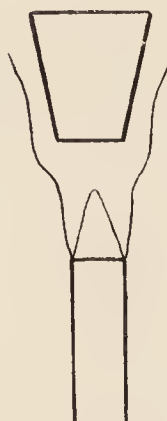


FIG. 46.

Correct Position
of Crucible in
Bunsen flame.

When a Bunsen burner is used for strongly heating a crucible, rather more air than is just required to produce a non-luminous flame should be admitted by means of the regulator; too much air, however, gives a noisy flame which is unsuitable. The position of a crucible in a Bunsen flame is important. If the crucible is placed so near the burner that the inner cone of unburnt gas impinges on it (Fig. 45), the bottom of the crucible will not become properly heated; and the crucible must not be enveloped in a large flame burning with a restricted air supply. The proper position, in which the bottom of the crucible is about half an inch above the top of the inner cone, is shown diagrammatically in Fig. 46. In order that the position of the crucible in the flame may be easily adjusted, the pipe-clay triangle on

which the crucible rests should be supported on a movable retort-stand ring.

The Méker Burner.—When a Bunsen flame is fully aerated, the volume of air passing into the burner is about 2.5 times the volume of the gas, whereas for the complete combustion of one volume of coal gas about six volumes of air are required. If a mixture of gas and air in the latter proportions were lighted at an ordinary burner, the flame would “strike back” and burn at the bottom of the tube.

In the Méker burner, the holes for the admission of air are large enough to pass sufficient air for the complete

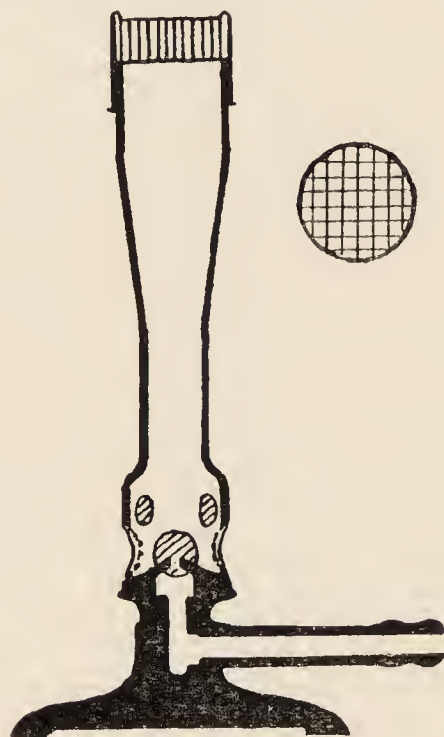


FIG. 47.

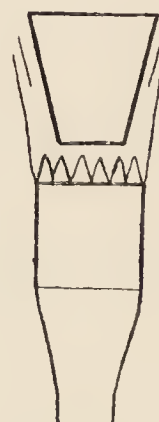


FIG. 48.

Correct Position
of Crucible in
Méker flame.

combustion of the gas, and a nickel grid is fitted into the top of the burner in order to prevent the flame striking back (Fig. 47). The flame of a Méker burner is smaller, and therefore hotter, than a Bunsen flame burning the same amount of gas, and the cold centre of unburnt gas is entirely absent. The hottest part of the flame is close to the nickel grid, but the temperature of the flame is much more uniform than that of a Bunsen flame. For igniting precipitates it is seldom necessary to use a blowpipe if a Méker burner is available.

Drying the Precipitate and the Filter.

It is often necessary to dry the precipitate and the filter before the latter is incinerated. To do this, first

remove the water in the stem of the funnel by means of filter paper; cover the mouth of the funnel with a piece of paper, the latter being folded over the rim of the funnel so that each fold overlaps the preceding one; and then place the funnel in the steam-oven in an upright position, and leave it there for several hours until the precipitate and paper are dry.

Incineration of the Filter.

In certain cases, the filter may be incinerated in presence of the whole precipitate; in others, the precipitate must be detached as far as practicable from the filter before the latter is incinerated. The procedure depends on the nature of the precipitate.

The filter must be incinerated apart from the precipitate (1) if the precipitate is fusible at the temperature of incineration, *e.g.* silver chloride, or (2) if the precipitate suffers reduction to the metallic state during the charring of the filter paper, *e.g.* silver chloride, lead sulphate, zinc carbonate, or (3) if the compound that is to be weighed is decomposed at the high temperature of the incineration, *e.g.* if calcium oxalate is to be converted into calcium carbonate, it must not be heated above dull redness.

The filter may be incinerated in presence of the precipitate in the case of (1) silica; (2) the oxides of iron, aluminium, chromium, and manganese; and (3) the sulphates of barium, strontium, and calcium.

The incineration is performed in a porcelain crucible, or in a platinum crucible if the use of the latter is permissible (see p. 143).

Tare of the Crucible.—Place the clean crucible, covered with the lid, on a pipe-clay triangle, and heat it to redness for a few minutes with a properly adjusted Bunsen flame. Remove the flame, and after about a minute lift the lid of the crucible with tongs, and place it temporarily on the desiccator cover, which is held inverted in the left hand; then remove the crucible and finally the lid to the desiccator. (Except on the ground rim, the desiccator cover must, of course, be free from grease.) Allow the desiccator to remain in the balance-room for twenty to thirty minutes, then weigh the crucible and lid, and afterwards replace them in the

desiccator. After the crucible has been heated and weighed, it must not be placed directly on the bench, but only on the pipe-clay triangle, in the desiccator, or (when cold) on a sheet of clean paper.

Incineration of the Filter in Presence of the Precipitate.

When this method is applicable, it is not necessary to dry the precipitate in the steam-oven; but large precipitates of chromic, ferric, and aluminium hydroxides may be partially dried as described on p. 150, before proceeding with the incineration.

Detach the filter very carefully from the funnel by means of a small spatula and remove it from the funnel. Fold the filter paper so as to form a small packet enclosing the precipitate, care being taken not to tear the paper. Place the packet in the weighed crucible and press it down gently. Remove any trace of the precipitate adhering to the funnel with a piece of "ashless" filter paper—first moistening the funnel, if necessary, by breathing into it—and drop this

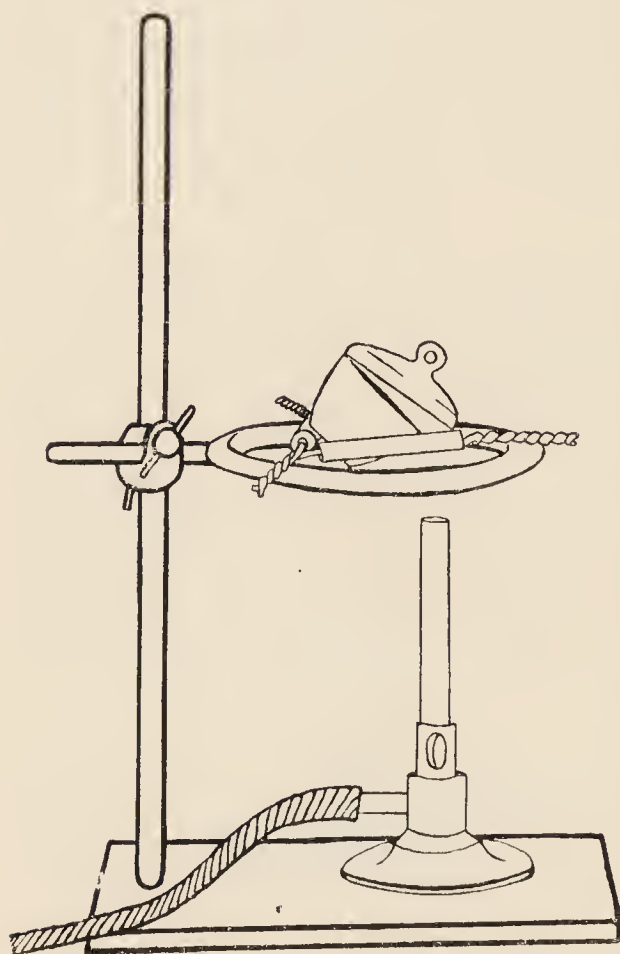


FIG. 49.

piece also into the crucible. Place the crucible on a pipe-clay triangle in a slanting position and cover it partially with the lid; the lid should rest partly on the triangle, as shown in Fig. 49, and a piece of platinum foil should be wrapped round the wire of the triangle at the point of contact with the lid.

Place a small ($\frac{3}{4}$ inch) flame under the crucible lid and about 1 inch from it, as shown in the figure. The hot gases are deflected into the crucible, and the contents soon become dry. When the paper begins to char, remove the lid of the crucible and place it, meanwhile, on a glazed tile

or a watch-glass. Place the crucible upright, and adjust the size of the flame and the distance of the crucible from it, so that the paper gradually chars without taking fire. If the paper should take fire, remove the flame and cover the crucible with the lid for a moment. When the escape of vapour ceases and the charring of the paper is complete, place the crucible *in a sloping position* again and heat more strongly until all the carbon is oxidised. If the carbon burns with difficulty, the oxidation may be accelerated by shifting the crucible into various sloping positions so that all parts that are blackened with carbon may become properly heated. A deposit of carbon is sometimes found on the under surface of the crucible lid, but this is easily removed by heating the inverted lid with the flame.

The precipitate is now ready for ignition, and the special instructions given for each should be followed. After igniting, remove the flame, wait for about a minute, then place the crucible in a desiccator and allow it to cool for twenty to thirty minutes. Weigh the crucible with its contents.

The ignition must be repeated as often as may be necessary until constant weight is attained. By "constant weight" is here meant that the difference between two consecutive weights is not more than two-tenths of a milligram, *i.e.* 0.0002 gram. The weighing must be performed as quickly as possible, especially if the precipitate is hygroscopic, and, when a weighing is repeated, all the weights used in the previous weighing should be placed on the balance before the crucible is removed from the desiccator. It is a mistake to leave an ignited precipitate in a desiccator for a long time, *e.g.* overnight, before weighing it; it should be re-ignited, and then weighed after cooling for not more than about thirty minutes.

Incineration of the Filter apart from the Precipitate.

The precipitate and filter must be thoroughly dried in the steam-oven. Two sheets (about 9 inches square) of glazed paper¹—white if the precipitate is coloured, and black if the

¹ The glazed paper must have clean-cut edges and be free from creases, and should be kept flat and unfolded between two pieces of cardboard.

precipitate is white—are laid on the bench. A shallow porcelain basin, about $2\frac{1}{2}$ inches in diameter, or a watch-glass of the same size, is placed on one of the sheets. The Bunsen burner or other metal apparatus, from which particles of rust or dirt are liable to drop, must not on any account be placed on the glazed paper.

Remove the well-dried filter from the funnel. Hold the filter over the glazed paper and loosen the precipitate by gently pressing the cone-shaped filter with the fingers. Transfer the bulk of the precipitate very carefully to the basin or watch-glass. Carefully unfold the filter and loosen the precipitate still adhering to it by lightly rubbing with the paper itself, care being taken, however, not to rub off any

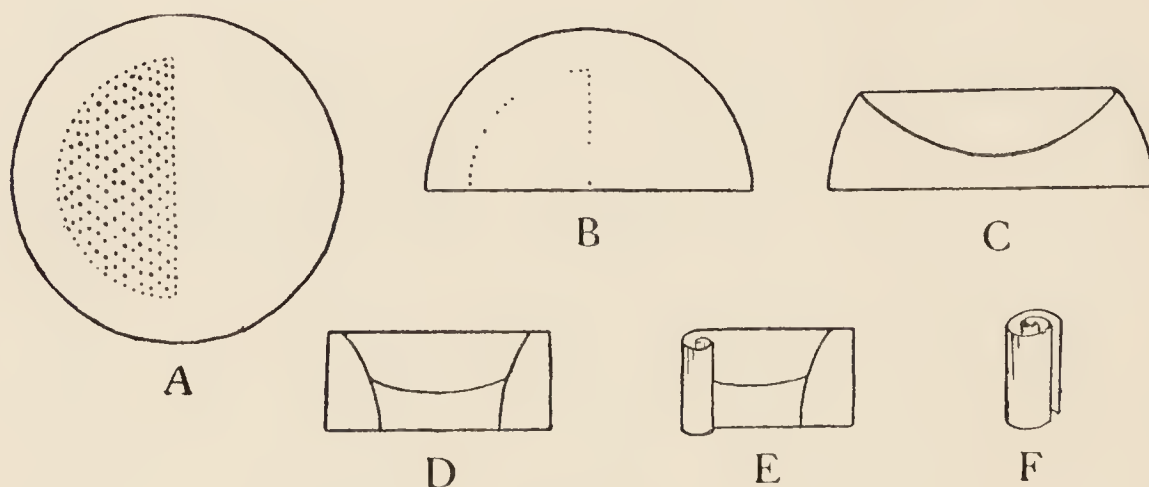


FIG. 50.

paper fluff. Empty this portion of the precipitate into the basin, then place the latter on the second sheet of paper, and cover the basin meanwhile with a clock-glass.

Fold the filter paper into a narrow strip, as shown in A to D (Fig. 50), the shaded portion in A representing the soiled part of the paper. Carefully wipe off any traces of the precipitate adhering to the funnel by means of the paper strip—first breathing into the funnel in order to moisten it—and then wrap up the strip into a compact roll, as shown in E and F. Place the roll in the weighed crucible which, meanwhile, is left in the desiccator.

If any precipitate has been allowed to fall on the glazed paper, transfer it very carefully to the basin by bending, but not folding, the sheet, and sweeping the particles into the basin by means of a small brush.

Now place the open crucible containing the filter on a pipe-clay triangle, and incinerate the filter in the manner described on p. 152. Allow the crucible to cool, and then treat the filter ash in accordance with the instructions given for the particular precipitate (see, for example, silver chloride or copper oxide). When the crucible is cold again, place it on the glazed paper, and very carefully transfer the main part of the precipitate to the crucible. Finally, dry or ignite the precipitate in the manner specified, and repeat the process until constant weight is attained.

Typical Gravimetric Exercises

The following section contains a number of simple exercises which have been so selected that they involve all the more important manipulative operations of gravimetric analysis. Each exercise can be performed with a salt which is readily obtainable in a state of purity, and the experimental result can therefore be checked by calculation. The value of the exercises as a preliminary training in gravimetric analysis is considerably greater if all the analyses are performed with solutions or solids of "unknown" composition. A list of solutions that are suitable for this purpose, with particulars as to their preparation, is given in the Appendix.

Most of the exercises given in this section should be carried out before the analyses described in later sections of the book are attempted. The exercises are arranged roughly in order of difficulty, except that, for convenience in description, the determination of aluminium has been placed immediately after that of iron, although it presents more difficulty than many of the other exercises.

Determination of Water in Magnesium Sulphate Heptahydrate.

OUTLINE OF METHOD.—A weighed quantity of the magnesium sulphate is heated to dull redness, and the loss of weight, which represents the water, is ascertained.

Procedure.—Heat a crucible and lid with a full Bunsen flame for five minutes. Remove the flame, allow the crucible to cool for about a minute, and then place it in a desiccator for half an hour. Weigh the crucible and lid accurately. Place about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in the crucible, and weigh again. Place the covered crucible,

resting on a pipe-clay triangle, about 6 inches above a small flame (not more than 1 inch high). At intervals of a few minutes, lower the crucible and increase the flame gradually until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about ten minutes. Allow the crucible to cool in a desiccator for half an hour, and weigh. Repeat the heating process until constant weight is attained.

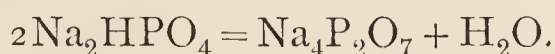
From the loss of weight, calculate the percentage of water in magnesium sulphate heptahydrate.

Determination of Water in Barium Chloride Crystals.

Weigh accurately in a tared porcelain crucible 1.5 to 2.0 grams of barium chloride crystals. Heat the crucible and contents to a temperature *not exceeding dull redness* until constant weight is attained (compare previous exercise). From the loss of weight, calculate the percentage of water in the barium chloride crystals.

Determination of Anhydrous Disodium Hydrogen Phosphate in the Crystalline Salt.

In a tared porcelain crucible weigh accurately about 0.5 gram of sodium phosphate (selected crystals free from efflorescence). Heat the crucible and contents for about an hour in the steam-oven, and then at a gradually increasing temperature with a Bunsen flame. Finally ignite at a red heat for about ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained. The residue is sodium pyrophosphate,



From the weight of sodium pyrophosphate obtained, calculate the percentage of anhydrous disodium hydrogen phosphate in the original crystals.

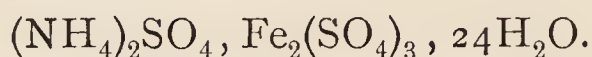
Determination of the Iron in Ammonium Iron Alum.

OUTLINE OF METHOD.—The salt is converted into ferric oxide by heating in a crucible, and the percentage of iron in the alum is calculated from the weight of the oxide obtained.

This method of determining iron is applicable only to compounds that leave a residue, after ignition, consisting of

pure ferric oxide. It cannot be used, therefore, for salts that contain a non-volatile impurity.

Procedure.—Weigh accurately in a tared crucible about 1.5 gram of ammonium iron alum,



Heat the covered crucible and contents very gently over a small flame; gradually increase the temperature until full redness is attained, and then continue the ignition with a Méker burner for fifteen minutes. Cool for one minute, transfer to the desiccator for twenty to thirty minutes, and weigh. Repeat the ignition and weighing until the weight is constant.

The result of the experiment should be recorded as follows:—

Weight of crucible and alum .	10.6842
Tare of crucible and lid . .	9.1722
Weight of alum taken . .	1.5120
Weight of crucible and Fe_2O_3 .	9.4241
” ” ” .	9.4234
” ” ” .	9.4234
Weight of Fe_2O_3 obtained .	0.2512

159.7 grams Fe_2O_3 represents 111.7 grams Fe, and the percentage of iron in the alum is therefore

$$\frac{0.2512 \times 111.7 \times 100}{159.7 \times 1.5120} = 11.61$$

Percentage of iron required by the formula = 11.58

Difference = +0.03

The error is 3 in 1158, or +0.26 per cent. This corresponds to 0.6 mgrm. of ferric oxide.

Other Examples of Analysis by Ignition.

Many other determinations may be carried out in the manner described in the last exercise. The method is easier and more expeditious than a precipitation method, but it is applicable only if the residue left after ignition is a pure substance, such as a pure oxide.

The residue left on ignition is usually an oxide. Before proceeding to the analysis, study the properties of the oxide in order to ascertain to what extent it may safely be heated; as a rule, this information may be obtained by reference to Part V. of this book.

The following are typical cases in which this method may be used :—

Aluminium in ammonia alum. The residue left after ignition is the oxide, Al_2O_3 .

Barium in barium peroxide and nitrate. The residue left after ignition is barium oxide, BaO .

Bismuth in bismuth oxynitrate and carbonate. The residue left after ignition is bismuth oxide, Bi_2O_3 .

Calcium in calcium acetate, hydroxide, carbonate, and nitrate. The residue left after ignition is calcium oxide, CaO .

Copper in copper hydroxide, carbonate, and nitrate. The residue left after ignition is cupric oxide, CuO .

Lead in lead hydroxide, peroxide, carbonate, and nitrate. The residue left after ignition is lead monoxide, PbO .

Zinc in zinc sulphate and basic carbonate. The residue left after ignition is zinc oxide, ZnO .

It is often possible, by slight modification of the procedure, to apply this method to other salts, *e.g.*—

- (1) The iron in ferrous ammonium sulphate may be determined by oxidation of a weighed sample with concentrated nitric acid and subsequent ignition. The residue obtained is ferric oxide.
- (2) Most sulphates are completely converted into oxides by repeated ignition, with addition of a few small pieces of solid ammonium carbonate before each ignition.

Determination of Iron as Ferric Oxide.

OUTLINE OF METHOD.—The iron, after oxidation to the ferric state if this should be necessary, is precipitated as ferric hydroxide by adding ammonia. The precipitate is filtered and washed. The filter is incinerated together with the precipitate, and the latter is converted into ferric oxide and weighed as Fe_2O_3 .

Ferric Hydroxide is a reddish-brown, flocculent precipitate, practically insoluble in water, in dilute alkalis, and

in ammonium salts, but readily soluble in acids. In order to obtain it free from basic salt, it should be precipitated by rapidly adding a moderate *excess* of ammonia to a cold or warm (but not boiling) solution, the latter being continuously stirred. If washed free from the last trace of soluble salts, ferric hydroxide occasionally passes through the filter in the form of a brown colloidal solution. This can be prevented by washing the precipitate with a 2 per cent. solution of ammonium nitrate instead of with water.

Ferric Oxide, obtained by strongly heating the hydroxide, is reddish-brown or almost black in colour, according to the temperature of the ignition. Contact with a reducing flame converts it partially into Fe_3O_4 , or even into metallic iron. If ferric oxide is ignited with ammonium chloride, ferric chloride volatilises. The ignited oxide dissolves very slowly in concentrated hydrochloric acid.

Exercise.—Weigh accurately, in a scoop or watch-glass, about 1.3 gram of ammonium ferric sulphate (ammonium iron alum). Transfer it to a 400 c.c. resistant-glass beaker, provided with a suitable clock-glass and stirring-rod (see Fig. 8, p. 23). Dissolve the salt in water, add 5 c.c. of dilute sulphuric acid, and determine the iron as follows.

Procedure.—Dilute to about 150 c.c., warm the solution and precipitate the iron as ferric hydroxide by rapidly adding a moderate excess of ammonia (15 to 20 c.c. of 2N solution), the solution meanwhile being continuously stirred. Leave the stirring-rod in the beaker, cover the beaker with the clock-glass, and heat the contents until boiling. Boil for about one minute, and make sure that ammonia is present in the escaping steam. Remove the flame, place the beaker on a paper mat, rinse the under side of the clock-glass with hot water, and allow the precipitate to settle.

Before commencing to filter the precipitate, read the general instructions regarding the filtration and washing of precipitates given on pp. 26 to 30.

Fit a $2\frac{3}{4}$ -inch (7 cm.) funnel with an 11-cm. paper. For this precipitate, the type of funnel shown in Fig. 19 on p. 30 and the open-texture variety of filter paper (p. 27 footnote) are preferable.

Begin the filtration by decanting as much as possible

of the clear liquid into the filter without disturbing the precipitate; pour the liquid down the stirring-rod, the latter being held against the rim of the beaker, and direct the liquid against the side of the filter and not into the apex (Fig. 15, p. 26). Do not fill the filter quite to the brim. Replace the beaker on the paper mat, add about 80 c.c. of hot water—pour the water against the side of the beaker in order to avoid loss by splashing—and stir well. Allow the precipitate to settle, and once more decant the clear liquid into the filter. Repeat this process three times.

Now transfer the precipitate to the filter by pouring as much of it as possible into the latter, and, by means of a jet of hot water, washing the remainder into the filter in the manner described on p. 28. Remove any traces of precipitate adhering to the beaker and stirring-rod by rubbing with a closely trimmed feather (or another stirring-rod tipped with rubber tubing), afterwards rinsing first the feather, and finally the beaker and the stirring-rod once more.

Any precipitate that cannot be removed in this way must be dissolved in dilute nitric acid (2 to 3 drops mixed with 1 c.c. of hot water), which is brought into contact with the entire surface of the beaker by means of the stirring-rod; a few drops of ammonia are then added in order to reprecipitate the ferric hydroxide, and the minute precipitate is collected in a separate *small* filter which is then carefully washed.

Finally, carefully scrutinise the beaker in a good light in order to make sure that no trace of precipitate remains.

The precipitate and filter paper must now be thoroughly washed with hot water in the following manner:—(1) Direct a fine stream of water against the filter paper—blowing gently at first in order that the impact of the water-jet will not cause a portion of the precipitate to be projected out of the funnel—and then, with a rotary motion of the wash-bottle jet, wash the precipitate as far as possible into the lower part of the filter. Allow the filter to drain completely, and repeat. (2) Direct the water-jet round the margin of the filter paper—which must be washed with great care—and then into the mass of the precipitate, which should be well churned up in the operation. Allow to drain, and repeat the washing until the filtrate is found to be free from sulphate. In order to

test for sulphate, rinse the end of the funnel-stem with water, and then collect about 5 c.c. of the filtrate in a test-tube; add a few drops of barium chloride solution, and warm. When no turbidity is observed, the washing is complete.

While the filtration is in progress, a clean crucible (porcelain or platinum) is ignited at a red heat, cooled in a desiccator for thirty minutes, and weighed. The filter, together with the precipitate, is then incinerated without previous drying, in the manner described on p. 152. When the incineration is complete, ignite the ferric oxide with a full Bunsen flame in the partially covered crucible for ten minutes, cool in a desiccator for thirty minutes, and weigh. Repeat the ignition until constant weight is attained.

From the weight of Fe_2O_3 obtained, calculate the percentage of iron in ammonium iron alum.

The following example shows how the weighings should be recorded, the result calculated, and the error stated:—

Weight of scoop + iron alum	. . .	6.8244
Weight of scoop	. . .	5.4474
Weight of iron alum	. . .	1.3770
Weight of crucible	. . .	15.2816
Weight of crucible + Fe_2O_3 (1st ignition)		15.5107
" " " (2nd ignition)		15.5102
" " " (3rd ignition)		15.5103
Weight of Fe_2O_3	. . .	0.2287

$$159.7 \text{ grams } \text{Fe}_2\text{O}_3 = 111.7 \text{ grams Fe.}$$

$$0.2287 \text{ gram } \text{Fe}_2\text{O}_3 = 0.2287 \times \frac{111.7}{159.7} \text{ gram Fe.}$$

$$\begin{aligned} \text{Percentage of iron found} &= 0.2287 \times \frac{111.7}{159.7} \times \frac{100}{1.377} \\ &= 11.61 \end{aligned}$$

Percentage of iron calculated
from the formula of iron

$$\text{alum} = 11.58$$

$$\text{Difference} . . . = + 0.03$$

$$\text{Error (3 in 1158)} . . = + 0.26 \text{ per cent.}$$

$$= + 0.6 \text{ mgrm. of } \text{Fe}_2\text{O}_3.$$

Determination of Aluminium as Oxide.

OUTLINE OF METHOD.—The aluminium is precipitated as aluminium hydroxide by means of ammonia in presence of ammonium chloride. The precipitate is converted into the oxide by ignition, and is weighed as Al_2O_3 .

Aluminium Hydroxide is a bulky, gelatinous precipitate, slightly soluble in ammonia, but almost insoluble in ammonia containing ammonium salts. Freshly precipitated aluminium hydroxide dissolves readily in dilute acids, but after keeping for some time it becomes almost insoluble. It is converted into alumina by ignition; a very high temperature is required for complete dehydration.

Aluminium Oxide (Alumina), obtained from the hydroxide by ignition, dissolves very slowly in hot concentrated hydrochloric acid. It may be brought into solution easily after fusion with potassium hydrogen sulphate. It is not decomposed or volatilised at the highest temperature attainable with a blowpipe flame.

Exercise.—Weigh accurately, in a scoop or a watch-glass, about 1.8 gram of ammonium aluminium sulphate, $(\text{NH}_4)_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$. Transfer it to a 400 c.c. beaker provided with a clock-glass cover and stirring-rod. Dissolve in water, and determine the aluminium as follows.

Procedure.—Dilute the solution to about 150 c.c. and add 10 c.c. of concentrated hydrochloric acid and 5 c.c. of concentrated ammonia (diluted with an equal volume of water). Heat until almost boiling, add 1 c.c. of methyl red indicator followed by dilute (2N) ammonia, drop by drop, until the solution becomes distinctly yellow (avoid excess). Boil for two minutes. Filter, and wash the precipitate in the same manner as described for ferric hydroxide (p. 161), but with a hot, 2 per cent. solution of ammonium nitrate instead of hot water.

Dry the precipitate (partially at least) in the steam-oven. Incinerate the filter in presence of the precipitate in a weighed platinum crucible (p. 152). Ignite with a full Bunsen flame for a few minutes and then for ten minutes with a Méker burner or a blowpipe. Cool, and weigh. Repeat the ignition until constant weight is attained.

Calculate the percentage of aluminium in the ammonium aluminium sulphate. Record all weighings and state the error of the result in the same way as shown on p. 162.

Determination of Chloride as Silver Chloride.

OUTLINE OF METHOD.—The chloride is precipitated as silver chloride by the addition of silver nitrate. The precipitate is filtered in the usual way, and, after incinerating the filter, is weighed as AgCl ; or, preferably, the precipitate is collected and weighed in a Gooch crucible.

Silver Chloride is not quite insoluble in water. At 18° , 1 litre of water dissolves 1.5 mgrm. It is much more soluble in hot water, 1 litre of which, at 100° , dissolves nearly 22 mgrms.; for this reason, a silver chloride precipitate must be washed with *cold water*. The solubility in very dilute hydrochloric and nitric acids and in dilute silver nitrate solution is very small; on the other hand, silver chloride is decidedly soluble in concentrated hydrochloric acid and in concentrated solutions of silver nitrate and most chlorides (1 litre of saturated sodium chloride solution dissolves 1 gram of silver chloride).

On exposure to sunlight, silver chloride loses chlorine, becoming first violet and then nearly black; and, although this change is at first superficial, the loss of weight is appreciable. Silver chloride melts at about 455° and volatilises appreciably.

Exercise.—Weigh accurately about 0.4 gram of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Transfer it to a 300 c.c. beaker, dissolve in water, and determine the chloride as follows.

Procedure.—Dilute the solution to about 100 c.c., and add 5 c.c. of dilute nitric acid. To the cold solution add silver nitrate solution gradually, while stirring briskly, until precipitation of the chloride is complete. A large excess of silver nitrate must not be added and is easily avoided, since the precipitate coagulates as soon as a small excess of silver nitrate is present. In order to protect the silver chloride from bright light, wrap a piece of brown paper round the beaker (use a rubber band to fix the paper in place). Place the beaker on the steam-bath, and stir the

liquid frequently until the precipitate has completely coagulated and the liquid is perfectly clear. Make certain that precipitation is complete by adding another drop of silver nitrate, and then allow the solution to cool.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate several times by decantation with cold water containing a few drops of nitric acid. (The nitric acid prevents the silver chloride becoming colloidal and passing through the filter.) Transfer the precipitate to the filter in the usual way, and wash with cold water acidified with nitric acid, until a portion of the filtrate gives no turbidity with dilute hydrochloric acid. Finally, wash with pure water until the filtrate is free from acid (test with litmus paper). Dry the precipitate in the steam-oven.

Incinerate the filter, apart from the precipitate, in a porcelain crucible in the manner described on p. 153. The carbon should be burned at as low a temperature as possible. By means of a glass rod, add 2 drops of concentrated nitric acid to the ash in the crucible and warm gently; then add 1 drop of concentrated hydrochloric acid and cautiously evaporate to dryness. (The object of this procedure is to convert into silver chloride the metallic silver produced during the incineration of the filter.) Transfer the precipitate to the crucible, and either heat the open crucible for five minutes with a very small flame, great care being taken not to fuse the precipitate, or dry the precipitate in the air-oven at 130° for an hour. Cool, and weigh.

A more convenient method of filtering silver chloride is by means of a Gooch crucible. The asbestos filter, is prepared in the manner described on p. 146, and the crucible is dried in the air-oven at 130° and weighed. After collecting and washing the precipitate in the crucible, the latter is again heated for an hour in the oven at the same temperature as before, and is then cooled and weighed.

From the weight of silver chloride obtained, calculate the percentage of chloride in the barium chloride.

Determination of Copper as Cupric Oxide.

OUTLINE OF METHOD.—The copper is precipitated as hydrated copper oxide by means of sodium hydroxide. The filter is incinerated apart from the precipitate, and the latter is converted into cupric oxide by ignition, and is weighed as CuO .

Copper Hydroxide, precipitated from a cold solution, is a light blue substance which becomes dark brown or black when boiled with the alkaline solution. The change in colour is due to loss of water, the composition of the black precipitate being probably $3\text{CuO} \cdot \text{H}_2\text{O}$. The precipitate is slightly soluble in sodium hydroxide solution, and readily soluble in ammonia and in dilute acids. Precipitation is incomplete in presence of organic matter or ammonium salts.

Cupric Oxide, produced from the hydrated oxide by ignition, is a black, hygroscopic powder, which remains unaltered at a red heat, provided reducing gases are carefully excluded.

Exercise.—Weigh accurately about 0.8 gram of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Transfer it to a 400 c.c. porcelain beaker or a large casserole, dissolve in water, and determine the copper as follows.

Procedure.—Dilute the solution to about 150 c.c. and heat until almost boiling. Remove the flame and add, drop by drop while stirring, a dilute solution of sodium hydroxide (see p. 167) until the precipitate becomes permanently dark brown or black. *A large excess of alkali must be carefully avoided*. Boil the contents of the covered vessel for about one minute, and then allow the precipitate to subside. Make certain that the clear liquid is alkaline by placing a drop on red litmus paper, afterwards rinsing the litmus paper into the vessel.

Decant the clear liquid through a 9-cm filter, and wash the precipitate several times with hot water by decantation. Transfer the precipitate to the filter. Wash the precipitate and the filter—especially the margin of the latter—until a portion of the filtrate gives no turbidity on boiling with 1 drop of dilute hydrochloric acid and 1 c.c. of barium chloride solution.

It frequently happens that a small quantity of the copper

oxide adheres to the side of the beaker and cannot be detached by rubbing with a feather or a rubber-tipped stirring-rod. In order to remove it, add 2 drops of dilute nitric acid, and bring the acid into contact with the entire surface of the beaker by means of the stirring-rod; rinse down the interior of the beaker with a very little hot water, heat the solution to the boiling-point over a minute flame, and reprecipitate the copper oxide by adding a few drops of sodium hydroxide (avoid excess). Transfer the minute precipitate at once to a separate *small* filter, and wash thoroughly.

Dry both filters and the precipitate very thoroughly in the steam-oven. Incinerate the filters, apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 153. When all the carbon is burned, allow the crucible to cool and moisten the ash with 2 drops of concentrated nitric acid in order to oxidise any reduced oxide formed during the incineration. Heat the crucible very gently with a minute flame until fuming ceases, and then heat to dull redness for about a minute. When the crucible has become nearly cold again, place it on glazed paper, and carefully transfer the main precipitate to the crucible.

Heat the copper oxide in the open crucible to dull redness for five minutes, cool in a desiccator as usual, and weigh. Repeat the ignition until constant weight is attained. During the ignition every care must be taken that reducing gases are excluded from the interior of the crucible, and for this purpose a perforated silica plate (p. 144), instead of a pipe-clay triangle, may be used to support the crucible.

From the weight of the copper oxide obtained, calculate the percentage of copper in the copper sulphate.

Note.—Pure sodium hydroxide, prepared from metallic sodium, must be used for the precipitation of copper oxide. In order to obtain it, cut about 0.5 gram of clean sodium into small pieces, and drop the pieces, one by one, into about 30 c.c. of water contained in a porcelain basin. Commercial sodium hydroxide (“purified by alcohol”) must not be used, because it contains traces of organic matter.

Determination of Zinc as Oxide.

OUTLINE OF METHOD.—The zinc is precipitated as basic carbonate by means of sodium carbonate. The filter is incinerated, apart from the precipitate, and the latter is converted into zinc oxide by ignition, and is weighed as ZnO.

Basic Zinc Carbonate, the composition of which varies according to the conditions of precipitation, is a white powder, very slightly soluble in water, and readily soluble in acids, alkali hydroxides, and ammonia. It is slightly soluble in sodium carbonate, and excess of the reagent must therefore be avoided. If the zinc solution contains much sulphate, sodium carbonate always precipitates some basic sulphate, and the precipitate, after filtration, must be dissolved again and reprecipitated; with a small amount of sulphate this is unnecessary. The basic carbonate is converted into zinc oxide by ignition.

Zinc Oxide is yellow when hot, but almost white when cold. It may be heated to bright redness without volatilisation; but if carbonaceous matter, such as traces of filter paper, is present, partial reduction to metallic zinc occurs, and the zinc volatilises readily.

Exercise.—Weigh accurately about 0.8 gram of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 300 c.c. porcelain beaker or casserole, dissolve in water, and determine the zinc as follows.

Procedure.—Dilute to about 100 c.c., and to the cold solution add sodium carbonate solution drop by drop until a faint turbidity appears; then heat until boiling. In this way the greater part of the zinc is precipitated as basic carbonate free from alkali carbonate. Now add 1 c.c. of phenolphthalein and more sodium carbonate until the solution becomes distinctly pink. Boil for several minutes.

After the precipitate has settled, decant the clear liquid through a 9-cm. filter, and wash the precipitate three times with hot water by decantation. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with hydrochloric acid and barium chloride (*cf.* p. 166).

Dry the precipitate and the filter in the steam-oven. Separate the precipitate as completely as possible from the filter, without, however, rubbing off any paper fluff, and wrap up the paper in the manner described on p. 154. In order to prevent as far as possible the reduction of any zinc oxide still adhering to the filter paper, moisten the paper with a few drops of ammonium nitrate solution, and dry it in the steam-oven for a few minutes. Incinerate the paper in a weighed porcelain crucible at as low a temperature as possible. When all the carbon is burned, add the precipitate, and heat the crucible, gently at first, and then to bright redness for ten minutes. Use a good oxidising flame and take care to exclude flame gases during the ignition, otherwise reduction of the oxide and loss of zinc (by volatilisation) will occur. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of zinc oxide obtained, calculate the percentage of zinc in zinc sulphate.

Note.—In order to avoid the risk of loss during the incineration of the filter, the zinc carbonate may be filtered by means of a Gooch crucible (see p. 145). The crucible containing the precipitate is dried in the steam-oven or air-oven, and is then placed in a larger platinum crucible and ignited with a full Bunsen flame.

Determination of Sulphate as Barium Sulphate.

OUTLINE OF METHOD.—The sulphate is precipitated as barium sulphate by the addition of barium chloride, and the precipitate, after ignition, is weighed as BaSO_4 .

Barium Sulphate, obtained by precipitation, is a fine, white powder which is not quite insoluble in water. At 18° , 1 litre of water dissolves 2.3 mgrms. It is from twenty to thirty times more soluble in cold dilute (normal) hydrochloric and nitric acids. It dissolves freely in concentrated sulphuric acid, but is reprecipitated on diluting the acid. In dilute sulphuric acid and in barium chloride solution it is practically insoluble. Barium sulphate may be ignited in air at a red heat without alteration of weight.

The marked tendency of barium sulphate to carry down traces of other substances contained in the solution is a common source of error in the determination of sulphate. The co-precipitated substances cannot always be removed by washing or ignition, and the results are accordingly high; sometimes loss of sulphuric acid occurs on ignition, and low results may be obtained. In order to reduce the error to a minimum, and to obtain a granular precipitate suitable for filtration, the following conditions must be observed:—

1. The solution must be free from iron (ferric), aluminium, chromium, nitrate, and chlorate. Iron can be removed by precipitation with ammonia; nitrate and chlorate by repeated evaporation with concentrated hydrochloric acid.
2. The solution should contain a little hydrochloric acid (about 2 per cent. by volume of the dilute acid), and its volume should not be less than 250 c.c. for each 0.5 gram of barium sulphate.
3. The barium chloride solution should be dilute (about 3 per cent.), and may be acidified with a few drops of dilute hydrochloric acid.
4. Precipitation must take place slowly, the hot barium chloride solution being added drop by drop to the nearly boiling sulphate solution, and an excess (about 5 c.c.) of the barium chloride should be introduced after the precipitation is complete.¹

Exercise.—Weigh accurately about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 400 c.c. beaker, dissolve in water, and determine the sulphate as follows.

Procedure.—Dilute the solution to about 250 c.c., add 5 c.c. of dilute hydrochloric acid, and heat until boiling. Prepare an approximately 3 per cent. solution of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), acidify about 30 c.c. of the solution with a few drops of dilute hydrochloric acid, and heat until boiling. Lower the

¹ If the barium chloride is added rapidly, the precipitate will contain an appreciable amount of chloride. After precipitation is complete, however, an excess of barium chloride may safely be added, in order to diminish the solubility of the barium sulphate.

flame under the magnesium sulphate solution until the latter just ceases to boil, rinse the cover glass into the beaker, and add the *hot* barium chloride solution drop by drop (see *Note* below); stir constantly while precipitation is in progress.

When the precipitation appears to be complete, allow the precipitate to settle, and ascertain whether the addition of a few more drops of barium chloride produces any further precipitate. If no turbidity appears immediately, make sure that there is none after waiting for a minute. (In order to avoid incomplete precipitation, particular care is necessary at this stage, since the precipitation of barium sulphate from a dilute solution is not visible immediately the reagent is added.) After all the sulphate is precipitated, add an additional 5 c.c. of barium chloride solution, stir briskly, and then set the beaker aside for about an hour.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate twice with hot water (by decantation). Transfer the precipitate to the filter. Wash the precipitate and the filter with hot water, until a portion of the filtrate gives no turbidity with a few drops of silver nitrate.

Incinerate the filter in a weighed crucible in the manner described on p. 152. After all the carbon is burned, allow the crucible to cool. In order to convert into sulphate any sulphide that may have been formed during the burning of the filter paper, add 2 or 3 drops of a mixture consisting of 1 c.c. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised, and then ignite with a full Bunsen flame for ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of barium sulphate obtained, calculate the percentage of sulphate (SO_4) in the magnesium sulphate.

Note.—A simple form of dropping tube, by means of which the barium chloride (or other reagent) can be added slowly, is made by drawing out a test-tube in the blowpipe flame so as to form a capillary through which the solution will pass at the rate of about 2 drops per second. The tube, charged with the hot barium chloride solution, is supported over the beaker in a clean clamp.

Determination of Magnesium as Pyrophosphate.

(*Precipitation as Magnesium Ammonium Phosphate.*)

OUTLINE OF METHOD.—The magnesium is precipitated as magnesium ammonium phosphate by means of sodium ammonium hydrogen phosphate and ammonia. The precipitate is converted into magnesium pyrophosphate by ignition, and is weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

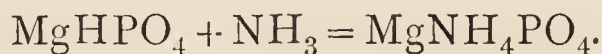
Magnesium Ammonium Phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is a white, crystalline substance which is somewhat soluble in water. At the ordinary temperature, 1 litre of water dissolves about 65 mgrms. It is much less soluble in ammonia.

In order to obtain a precipitate of normal composition (MgNH_4PO_4), the solution must be neutral and as free as possible from ammonium salts, excess of phosphate must be avoided, and the ammonia must be added last. If the precipitation takes place in presence of much ammonia or ammonium salt, the precipitate contains $\text{Mg}_3(\text{PO}_4)_2$ or $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate, whereas the precipitate of normal composition, MgNH_4PO_4 , is converted into magnesium pyrophosphate.

The microcosmic salt ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) precipitates amorphous magnesium hydrogen phosphate,



and ammonia converts this into crystalline magnesium ammonium phosphate,



If the precipitation takes place in presence of much potassium or sodium salt, the precipitate is contaminated with magnesium potassium (or sodium) phosphate. If much ammonium, potassium, or sodium salt is present, a "double precipitation" is necessary; the procedure is described on p. 284.

On heating to 100° , magnesium ammonium phosphate loses 5 molecules of water; above 200° , it is converted into magnesium pyrophosphate.

Magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, is unchanged by ignition in air, but if reducing gases have access, phosphorus

and volatile phosphorus compounds escape, and normal magnesium orthophosphate is formed. Magnesium pyrophosphate fuses about 1220° .

Exercise.—Weigh accurately about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 300 c.c. beaker, dissolve in water, and determine the magnesium as follows.

Procedure.—Dilute the solution to about 100 c.c. and heat until boiling. Add to the boiling solution, drop by drop, a moderate excess of a freshly prepared 5 per cent. solution of microcosmic salt (15 to 20 c.c.). Allow the solution to cool, add 25 c.c. of ammonia, and stir briskly. Cover the beaker and set it aside for two to three hours.

Decant the clear solution through a filter; use an 11-cm. paper if the precipitate is bulky. Wash the precipitate twice by decantation with dilute ammonia (25 c.c. of 2N ammonia diluted to 100 c.c.). Transfer the precipitate to the filter, and wash with dilute ammonia until a portion of the filtrate gives no turbidity with dilute hydrochloric acid and barium chloride. Dry the precipitate in the steam-oven.

Incinerate the filter, apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 153. Carbonise the paper and burn the carbon *at as low a temperature as possible*. If the carbon burns with difficulty, allow the crucible to cool, and moisten the contents with 2 drops of concentrated nitric acid. Evaporate the acid carefully, and then heat more strongly until the ash is perfectly white. Allow the crucible to cool again, and add the precipitate. Heat the crucible gently until ammonia is no longer evolved, gradually increase the temperature, and finally heat for ten minutes with a Méker burner. Cool, and weigh. Repeat the ignition until constant weight is attained.

It is preferable to collect and weigh the precipitate in a Gooch crucible (see p. 145). After washing the precipitate with dilute ammonia (six to eight times should suffice), the crucible, containing the precipitate, is dried in the steam-oven, and is then placed in a larger platinum crucible and ignited with a full Bunsen flame.

From the weight of magnesium pyrophosphate obtained, calculate the percentage of magnesium in magnesium sulphate.

Determination of Copper as Cuprous Sulphide.

OUTLINE OF METHOD.—The copper is precipitated as cupric sulphide by means of hydrogen sulphide. The filter is incinerated apart from the precipitate, and the latter is converted into cuprous sulphide by heating in a current of hydrogen, and is weighed as Cu_2S .

Cupric Sulphide is a black precipitate practically insoluble in water, in hydrochloric acid (5N), and in sulphuric acid. It dissolves readily in nitric acid, with separation of sulphur. Exposed to the air in a moist state, it oxidises rapidly, acquires a greenish colour, and becomes soluble in water. In order to prevent oxidation, the precipitate must be washed with water containing hydrogen sulphide. Heated in a current of hydrogen, cupric sulphide is converted into *cuprous sulphide* which, if air is excluded, may be ignited at a dull red heat without decomposition.

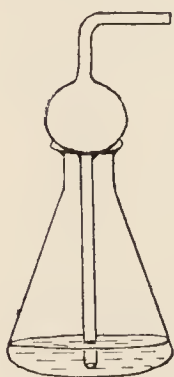


FIG. 51.

Exercise.—Weigh accurately about 0.8 gram of copper sulphate. Transfer it to a 300 c.c. conical flask, dissolve in water, and determine the copper as follows.

Procedure.—Dilute the solution (which must not contain nitric acid or nitrates) to about 150 c.c., add 3 c.c. of concentrated sulphuric acid, and heat the solution nearly to the boiling-point. Pass a slow current of hydrogen sulphide through the hot solution until the precipitate is quite black and settles quickly and the supernatant liquid is clear and colourless. The rate at which hydrogen sulphide is absorbed is greatly increased if the gas-inlet tube is expanded into a bulb (Fig. 51) so that the mouth of the flask is almost completely closed. The precipitation requires at least half an hour.

Meanwhile, prepare some hydrogen sulphide solution by passing the gas into water contained in a special wash-bottle fitted with a valve (Fig. 17, p. 29).

When precipitation is complete, remove the gas-delivery tube and rinse it into the flask; rub off any adhering precipitate by means of a prepared feather, and rinse the tube again, internally as well as externally, and also the feather.

Decant the clear liquid through a 9-cm. filter, and, with the help of the hydrogen sulphide solution, transfer the precipitate at once to the filter. Wash the precipitate and the filter, especially the margin of the latter, with hydrogen sulphide solution, until a portion of the filtrate is found to be free from acid when tested with a drop of methyl orange. During the whole process of filtration and washing, the precipitate must be kept covered with the washing liquid as far as possible; if this is not attended to, partial oxidation and solution of the precipitate will occur, and the filtrate will become turbid and acquire a greenish colour.

Dry the precipitate in the steam-oven. Incinerate the filter apart from the precipitate in a weighed Rose crucible (p. 147). Having made sure that no carbon remains unburned, allow the crucible to cool, introduce the main precipitate, and also a little (about 0.01 gram) finely powdered, *pure* sulphur. Pass a current of pure dry hydrogen (see p. 147) into the crucible at the rate of about four bubbles per second, and heat the crucible, gently at first, and then to dull redness for ten minutes. The excess of sulphur volatilises, and the cupric sulphide is converted into cuprous sulphide. Remove the flame and at the same time increase the rate of the gas current somewhat, and allow the crucible to cool. (Make sure that the hydrogen no longer burns at the crucible by pinching the rubber connection for an instant.) When the crucible is almost cold, transfer it to a desiccator for ten minutes, and then weigh it. Repeat the ignition in the same way until constant weight is attained.

The cuprous sulphide must appear blue-black or black; if any red-brown particles are visible (metallic copper or cuprous oxide), the current of hydrogen during cooling was too slow or the temperature of ignition too high, and the ignition with sulphur must be repeated.

From the weight of cuprous sulphide obtained, calculate the percentage of copper in the copper sulphate.

Note.—The precipitate may be ignited with sulphur in a current of pure, dry carbon dioxide (p. 148) instead of hydrogen.

Determination of Calcium as Oxalate.

OUTLINE OF METHOD.—The calcium is precipitated as calcium oxalate by means of ammonium oxalate, and the precipitate, after conversion into calcium oxide or calcium sulphate, is weighed as CaO or CaSO_4 .

Calcium Oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is a fine, white powder which is very slightly soluble in water. At 18° , 1 litre of water dissolves about 6 mgrms. It is more soluble in hot water; at 95° , 1 litre of water dissolves about 14 mgrms. In dilute ammonia it is somewhat less soluble than in water. It dissolves easily in hydrochloric and nitric acids, but very sparingly in acetic acid. It is somewhat soluble in magnesium chloride solution. Dried at 100° , the precipitate has the composition of the monohydrate; if heated to a temperature approaching dull redness, it is converted into calcium carbonate.

Calcium Carbonate may be heated to about 500° without appreciable decomposition. The dissociation pressure increases (slowly at first and then rapidly) with the temperature, and becomes equal to the atmospheric pressure at about 812° . If heated above 800° in a vessel from which the carbon dioxide can escape, it is completely converted into calcium oxide.

Calcium Oxide is a hygroscopic substance, and should be exposed to the air as little as possible during weighing. As it also absorbs carbon dioxide readily, it should be kept in a desiccator containing soda-lime or sticks of sodium hydroxide.

Calcium Sulphate remains unaltered at a dull red heat. Slow decomposition, with loss of sulphur trioxide, occurs at bright redness.

Exercise.—Weigh accurately 0.4 to 0.5 gram of powdered calcite (calcspar). Transfer it to a 400 c.c. beaker. Add about 10 c.c. of water, cover the beaker with a clock-glass, and dissolve the calcite by adding dilute hydrochloric acid (about 10 c.c.). Dilute with a little water, and boil the solution for a few minutes in order to free it from carbon dioxide. Determine the calcium as follows.

Procedure.—Add a few drops of methyl orange, and carefully neutralise the solution with ammonia. Then add 1 c.c. of dilute hydrochloric acid, dilute the solution to about 200 c.c., heat until boiling, and add a moderate excess of a boiling solution of ammonium oxalate (freshly prepared cold saturated solution). Then make the mixture alkaline with ammonia, and boil for a few minutes. Set the beaker aside for one hour.

Filter through a 9-cm. paper, and wash the precipitate three times by decantation with cold, dilute ammonia (25 c.c. of 2N ammonia diluted to 100 c.c.), or with a 1 per cent. ammonium oxalate solution. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with nitric acid and silver nitrate. (Avoid excessive washing with water, especially hot water, on account of the appreciable solubility of the precipitate.)

(1) *If the precipitate is to be converted into and weighed as calcium oxide*, incinerate the filter, together with the still moist precipitate, in a weighed platinum crucible, in the manner described on p. 152. After all the carbon is burned, heat the crucible, gently at first, and then with a Méker burner for twenty minutes. Cool, and weigh. Repeat the ignition (for ten minutes) until constant weight is attained.

(2) *If the precipitate is to be weighed as calcium sulphate*, a porcelain or silica crucible may be used. Proceed as in (1), but ignite with a Méker burner for five minutes only. Cool, and then slake the calcium oxide by pouring about 1 c.c. of water into the crucible. (The water must be added all at once, not drop by drop.) Then add an excess (about 10 drops) of concentrated sulphuric acid. Heat the crucible in an air-bath (Fig. 14, on p. 25), gently at first and then with a full Bunsen flame, until the excess of sulphuric acid has been volatilised. Ignite the dry sulphate at low redness, cool, and weigh. Repeat the treatment with acid (add a few drops only), etc., until constant weight is attained.

Electrolytic Methods

Electrolytic methods are confined almost entirely to the determination of metallic radicals and, as a rule, the metal is deposited as such on the cathode. In the case of lead, it is found better so to adjust the conditions of electrolysis that the lead is deposited as lead dioxide on the anode. If a metal is to be determined electrolytically, it must (1) be deposited in a pure state; (2) be deposited completely from the solution; and (3) form a coherent deposit on the electrode.

The nature of the deposit and the accuracy of the determination depend on a number of conditions, among which are the rate of deposition, the composition of the solution, and the temperature. The correct conditions vary for different metals and must be adjusted for each metal within fairly narrow limits. Two most important factors are the current voltage and the current density. Current density is the amount of current, measured in amperes, per 100 sq. cm. of cathode surface immersed in the solution. Thus, if a current of 1.5 ampere is used and the area of cathode immersed is 75 sq. cm., the current density is $1.5 \div 0.75 = 2$.

Separations.—It is often possible to separate metals from one another quantitatively by electrolytic methods. The separation may be effected in two ways: (1) by suitable adjustment of the voltage; or (2) by suitable alteration of the composition of the solution. In order to illustrate this, two methods used to separate copper from nickel may be mentioned:—

1. The copper is deposited from a solution of the mixed sulphates by electrolysis with a 2-volt current (with this voltage, no nickel is deposited); after the copper

has been removed, the nickel may be deposited by using a higher voltage.

2. The same separation may be effected with a fixed voltage (say 4 volts). The copper is first deposited in presence of nitric acid; when the copper has been removed, the nickel is deposited by further electrolysis after eliminating nitrate and adding an excess of ammonia to the solution.

Composition of the Solution.—Sulphates and nitrates are often the best electrolytes, but it is sometimes necessary to

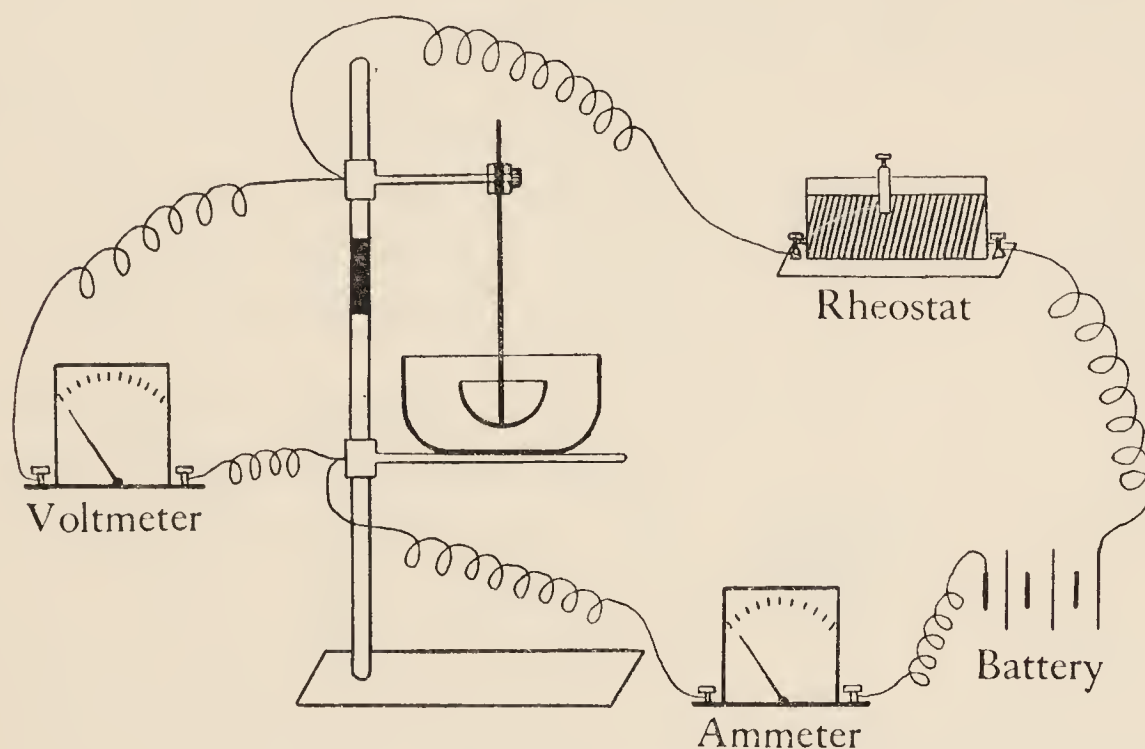


FIG. 52.—General Arrangement of the Apparatus.

use solutions containing complex salts, such as “double” oxalates, tartrates, or cyanides, in order to obtain satisfactory and complete deposition of the metal. The concentration of acid present is often an important condition, especially in securing the separation of metals. The presence of hydrochloric acid, or of a chloride in an acid solution must be avoided, since the chlorine liberated at the anode will attack the platinum. If chloride is present, it should be expelled by evaporating the solution with concentrated sulphuric acid.

Source of Current.—By far the most satisfactory source of current for this work is a battery of lead accumulators capable of giving up to 5 amperes at an E.M.F. of 2 to 10 volts. The voltage of the accumulators must be tested from

time to time. It is not advisable to run an accumulator after the voltage has fallen below 1.9 volt. Batteries of Bunsen or Daniell cells may also be used, but are less convenient than accumulators.

Electrodes. — For some purposes, a platinum basin holding about 150 c.c. of liquid is a convenient cathode. The inner surface should be roughened (suitable basins with the surface roughened by a sand-blast may be purchased) in order that the deposit may adhere firmly. This roughened surface must never be cleaned with sand or other abrasive material. As anode, a stout perforated platinum disc, shaped like a saucer (Fig. 53), may be used, or a stout platinum wire



FIG. 53.



FIG. 54.

may be wound in a flat spiral as shown in Fig. 54. The stout platinum wire D is used to clamp the electrode in position and to make the electrical connection.

It is sometimes inconvenient to use a platinum basin to contain the electrolyte and to serve as cathode, *e.g.* in case it is necessary to remove the electrolyte and wash the deposit without interrupting the current (see p. 181). Instead of the basin electrode, the cathode may take the form of a cylinder of platinum gauze which is suspended, together with the anode, in a beaker containing the electrolyte. When the deposition is complete it is easy, with this arrangement, to remove the cathode and simultaneously to rinse it with water—without previously interrupting the current; or, instead, the beaker containing the electrolyte may be removed and another beaker, containing water, immediately substituted.

The use of a rotating cathode is described on p. 183.

Stand.—A stand with insulation between the positive and negative terminals is convenient for use with a basin electrode; if a special stand is not available, the necessary insulation may be obtained by clamping the anode support D in a rubber cork.

Siphon.—When the deposition is complete, it is often necessary to remove the electrolyte without stopping the current, otherwise partial re-resolution of the deposit would occur. This is most easily accomplished in the case of a basin electrode by means of a siphon arranged as shown in Fig. 55. The short limb of the siphon should reach to the bottom of the basin, and to prevent abrasion it should be covered with a short piece of rubber tubing. The longer limb should be fitted with a rubber tube and spring-clip by means of which the rate of outflow may be regulated. To start the siphon, fill it with water, place it in position, and open the clip. Run water into the basin from a tap-funnel to replace the solution withdrawn. The water must be allowed to flow gently on to the surface of the solution so that there is as little mixing as possible. When about 200 c.c. of water has been used, stop the current, disconnect the apparatus, and complete the washing in the usual manner with the wash-bottle.

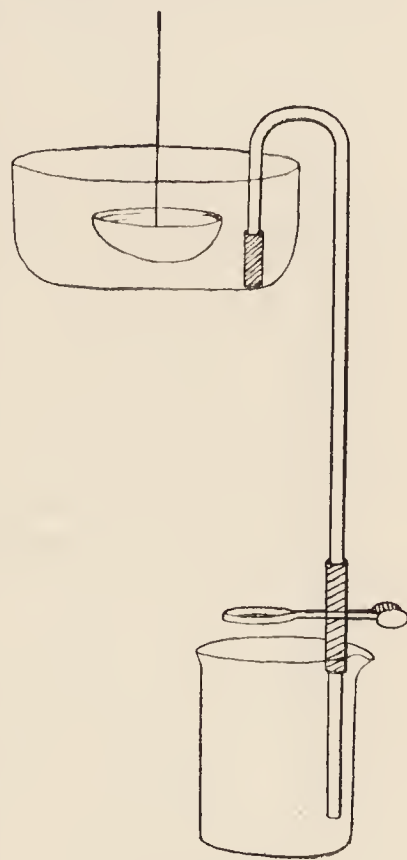


FIG. 55.

Measurement of Current.—An ammeter reading up to 5 or 6 amperes (not necessarily very accurately) and a high resistance voltmeter recording up to 10 volts are required.

Regulation of Current.—It is necessary to have some form of adjustable resistance, such as a rheostat with a sliding contact, in the circuit. A rheostat with a maximum resistance of 10 ohms will be found suitable for most purposes.

Electrolytic Determination of Copper.

(With Stationary Electrodes.)

Copper is readily deposited from a copper sulphate solution by electrolysis, and forms a coherent deposit if the potential used is not above 2.2 volts. Further, the copper under these conditions is deposited in a pure state, even

when the solution contains iron, nickel, and other metals. The time required for complete deposition is greatly increased when iron is present in the solution, but the precipitation is almost quantitative, even in presence of 1 gram of iron, if sufficient time is allowed. Nitrate and chloride interfere with this method, and if these radicals are present the solution must be evaporated with concentrated sulphuric acid until complete conversion into sulphate is effected.

Procedure.—Clean the platinum basin with sodium hydroxide in order to remove grease, then with nitric acid, and finally with water. Drain the basin—but do not touch the interior with the fingers or wipe it with a cloth—place it in the steam-oven for half an hour, cool (without using a desiccator), and weigh.

Dilute the solution to 100 c.c., and, if there is not some free sulphuric acid already present, add 5 c.c. of dilute sulphuric acid. Place the solution in the tared platinum basin, and use an anode of sheet platinum or stout platinum wire. Cover the basin with a clock-glass cut into two pieces and provided with a notch for the anode wire. Connect the electrodes with an accumulator, without any intermediate resistance, and allow the current to pass for about twelve hours. It is often convenient to start the experiment late in the day and allow the current to pass all night.

Next morning, rinse the drops on the under side of the clock-glass into the basin and allow the electrolysis to continue for another hour. Switch off the current, remove the anode and rinse it quickly, and immediately pour the solution into a beaker. Without delay, rinse the basin several times with water, and then twice with alcohol (reject the alcohol washings). Dry the basin in the steam-oven for not more than ten minutes, then cool, and weigh.

Remove the deposit from the basin by means of hot, dilute nitric acid, and weigh the clean, dry basin again. Pour back the solution and pass the current again for an hour, and re-weigh. (Any further deposit of copper will be readily seen on the clean surface of the platinum.) If the weight is unchanged, it may be assumed that all the copper is deposited. If, however, large quantities of other metals (particularly iron) are present, the solution may still contain copper.

The results obtained by this method are consistently low by about 1 mgrm. The last trace of copper may be removed by increasing the potential to 4 volts for the last half hour, but this is not always permissible.

Electrolytic Determination of Copper.

(With a Rotating Cathode.)

If the deposit of copper is to be adherent, it is essential that there should be no simultaneous liberation of hydrogen at the cathode. The evolution of hydrogen may be prevented in two ways:—(1) By using a current not exceeding 2.2 volts—the evolution of hydrogen at this voltage being negligibly small. (2) By electrolysis in presence of nitric acid—the nitric acid acting as a depolariser; this method is more generally useful than the first, since nitric acid is the acid usually employed to dissolve copper alloys.

The time necessary for complete deposition is always greatly shortened by using a rotating electrode; and this device is particularly useful when copper is to be deposited from a solution containing nitric acid, since it prevents local accumulation of nitrous acid at the cathode.

The following method for the determination of copper is convenient and accurate, and it may be used to separate copper from tin, nickel, zinc, and iron. The solution must contain from 5 to 10 per cent. of nitric acid. It must be free from chloride and nitrite, both of which may be removed, if necessary, by evaporation with sulphuric acid.

The main difficulty in this method is to prevent re-solution of copper during the washing process; this is due to the presence of *nitrous* acid, formed by electrolytic reduction of the nitric acid. If the nitrous acid is destroyed by adding a little hydrogen peroxide or urea, just before interrupting the current, no copper is redissolved by the nitric acid.

Apparatus.—The general arrangement of the apparatus is shown in Fig. 56. The electrolysis is conducted in a deep, narrow beaker (200 c.c.) held rigidly in position by a large clamp (not shown in diagram). The copper is deposited on a tared, stout, gold or platinum wire arranged in a spiral as shown in Fig. 56. The spiral is fixed into the glass tube

forming the spindle of the wooden pulley by means of a small cork at the upper end. The wire projects through this cork and a small brass cap (a binding screw) is fixed on it. A brass spring, or a small brush made from brass wire, which presses lightly on this cap, serves to connect the rotating cathode with the negative pole of a 10-volt battery (five accumulator cells in series). The brass cap protects the cathode itself from abrasion. A disc of stout platinum, or a piece of foil attached to a stout platinum wire, forms the anode. If platinum foil is used, it should be held flat against the side

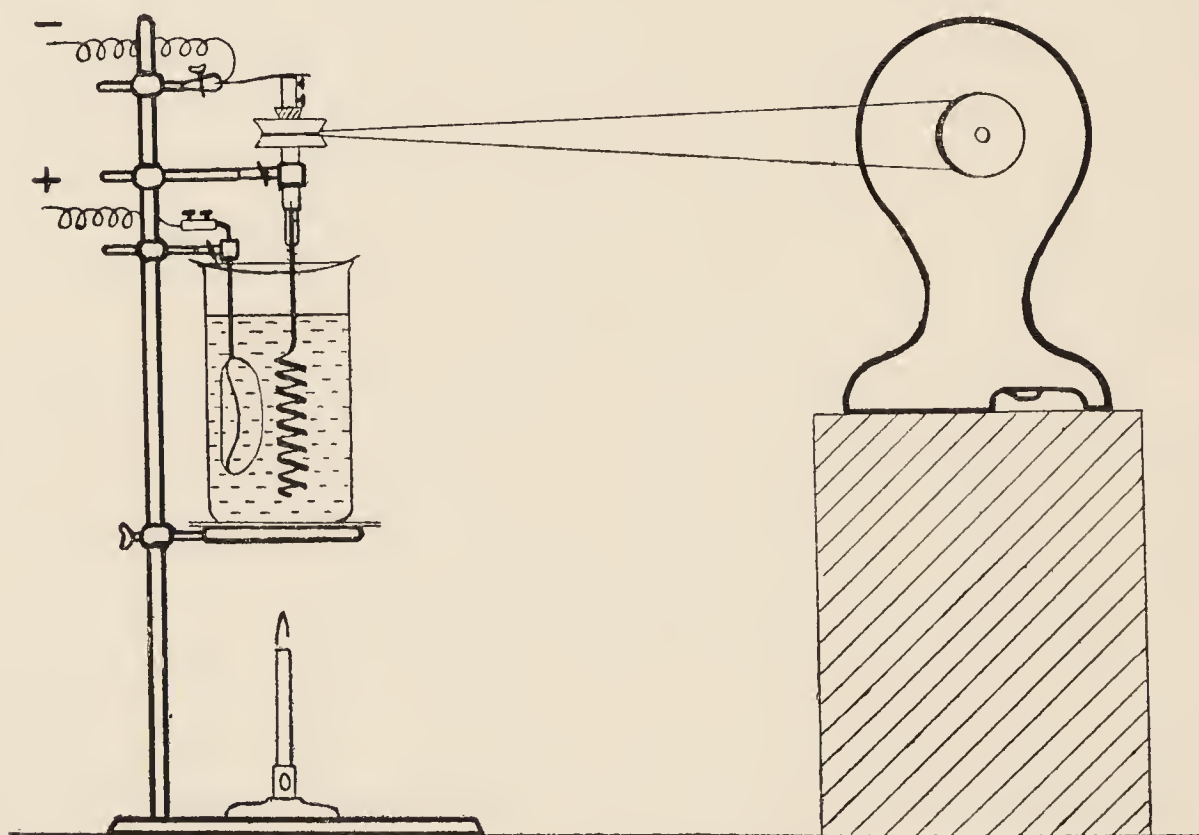


FIG. 56.—General Arrangement of the Apparatus with a Rotating Electrode.

of the beaker by means of two \cap -shaped pieces of glass rod, so that there is no chance of it touching the rotating cathode. The beaker is covered with a split clock-glass provided with openings through which the electrodes pass. The apparatus must be supported on *two* stands—one very rigid stand for the rotating cathode and the brass spring, and another for the beaker and the anode. (In order to simplify the diagram, only one stand is shown.) The cathode is rotated at a high speed by means of a small electric motor or a hot-air engine.

Procedure.—Use sufficient of the material to yield, preferably, about 0.25 gram of copper. Place the solution in the beaker, add 5 c.c. of dilute sulphuric acid, and dilute to

150 c.c. Then add sufficient nitric acid to bring the concentration of that acid up to about 5 per cent., *i.e.* add 8 c.c. of the concentrated acid if the solution originally contained none. Before closing the circuit, start the cathode rotating, and make sure that it does not touch either the anode or the side of the beaker. Pass a current of about 0.5 ampere at first, and after a few minutes increase it until from 2 to 5 amperes are passing. The maximum current that may be used without causing loose or black deposits depends on the speed at which the cathode is rotating and on its surface. The time necessary for complete deposition depends on many variable factors; with a solution containing copper alone, about one hour is required, using the apparatus described and a current of 2.5 amperes; in presence of nickel, two hours are necessary.

A short time before stopping the electrolysis, rinse the clock-glass covering the beaker. When the deposition is complete, add about 2 c.c. of hydrogen peroxide or 1 gram of urea. Reduce the current to about 0.5 ampere and then stop the motor. Lower the beaker and simultaneously rinse the cathode with a jet of water; also rinse the anode. Remove the cathode and rinse it with alcohol. Dry it in the steam-oven for a few minutes, and weigh.

Until experience as to the time necessary for complete deposition has been gained, the solution must be again electrolysed. (The cathode should be cleaned with hot, dilute nitric acid, dried and re-weighed before using it again.) Traces of copper may be tested for by adding sodium acetate and hydrogen sulphide to a small portion of the solution. If it is found to contain copper, evaporate the test portion almost to dryness, add a few drops of nitric acid to dissolve the copper sulphide, and return the solution to the beaker.

Electrolytic Determination of Nickel.

If copper is present in the original solution, it must be removed by depositing from an acid solution, as already described. If nitrate is present, it must be removed by evaporation with concentrated sulphuric acid. Chloride and sulphate do not interfere with the process.

Procedure.—The amount of substance taken should preferably be such as will yield about 0.3 gram of nickel. Make the solution approximately neutral, add 5 grams of ammonium sulphate and 20 c.c. of concentrated ammonia, and dilute to about 120 c.c.

The arrangement of the apparatus should be exactly as described above for the determination of copper with a rotating cathode, except that the beaker containing the solution must be supported above a wire gauze.

By means of a small flame, raise the temperature of the solution to 60° — 80° , and keep it between these limits during the electrolysis. The electrode potential difference should be from 3 to 4 volts (three or four accumulator cells) and the initial current about 0.5 ampere. Increase the current gradually to about 2 amperes. When the solution is colourless, test for nickel in a small portion (5 c.c.) by addition of hydrogen sulphide. The electrolysis takes about one hour.

When all the nickel is deposited, reduce the current to about 0.5 ampere, and then stop the motor. Lower the beaker and at the same time rinse the electrodes with a jet of water. Remove the cathode, rinse it with alcohol, dry it in the steam-oven for a few minutes, and weigh.

Exercise.—Determine the percentages of copper and nickel in a German "nickel" coin. Dissolve a weighed portion (about 0.6 gram) in 15 c.c. of concentrated nitric acid mixed with an equal volume of water. Boil the solution for a few minutes, and dilute to 120 c.c. Electrolyse the acid solution, using a rotating cathode, and weigh the copper deposit. After removal of the copper, evaporate the solution with sulphuric acid to remove nitrate, and determine the nickel as described above.

Electrolytic Determination of Cadmium.

Cadmium is readily deposited electrolytically from solutions of most cadmium salts, but in order to obtain a pure coherent deposit it is best to use a solution of potassium cadmium cyanide.

Procedure.—To the cadmium solution add 1 c.c. of phenolphthalein solution, and then add pure sodium hydroxide

solution until a permanent pink coloration is produced. Prepare a dilute solution (about 5 per cent.) of potassium cyanide and add this to the cadmium solution, with constant stirring, until the precipitate has redissolved. A fair excess of potassium cyanide beyond that necessary to dissolve the precipitate is advantageous.

Dilute to about 120 c.c. and electrolyse in a tared platinum basin, arranged as shown in Fig. 52 on p. 179. The electrode potential difference should be about 5 volts (three or four accumulator cells), and the initial current about 0.5 ampere. After five to six hours' electrolysis with this current, increase the current to 1.0—1.2 ampere, and continue the electrolysis for another hour. Test a small portion of the solution (5 c.c.) for cadmium by adding hydrogen sulphide.

When the deposition is complete, stop the current, pour off the liquid *at once*, and rinse the basin immediately with water; then rinse with alcohol, and finally with ether. Dry for a few minutes in the steam-oven, cool, and weigh.

Electrolytic Determination of Lead as Dioxide.

The conditions of electrolysis are so adjusted that the lead is deposited as lead dioxide on the anode. The only metal that interferes with this method is manganese. Chloride must be absent.

Procedure.—Clean, dry, and weigh a platinum basin. Measure the solution into the basin, add 15 c.c. of concentrated nitric acid, and dilute to 100 c.c. Connect with an accumulator, through an adjustable resistance and an ammeter, making the dish the *anode*, and pass a current of about 0.05 ampere for twelve to fourteen hours, or overnight. Then, without interrupting the current, remove the acid liquid by means of a siphon, and at the same time run distilled water into the basin from a tap-funnel, care being taken that the deposit of lead dioxide remains under the surface of the liquid during the operation.

Continue washing until the liquid is almost free from acid, then stop the current, rinse the basin with distilled water, and dry in the air-oven at 180° to constant weight. The lead

dioxide retains traces of water even at 180° and the results are somewhat high. It is advisable, therefore, to heat the basin gently in order to convert the lead dioxide into lead monoxide, care being taken to avoid contact with a reducing flame, and then to weigh again.

The electrolysis may be completed in a shorter time by heating the solution to about 60° , and using a current of 1 to 1.5 ampere.

Removal of the Deposit.—Warm the lead oxide or dioxide with moderately concentrated nitric acid to which a little glucose has been added; or warm it with potassium nitrite solution acidified with nitric acid.

PART IV

COLORIMETRIC METHODS

THE accurate determination of a very small quantity, or of the merest trace, of a substance is frequently of the highest importance, and it is often found that the most accurate and by far the easiest method is a colorimetric one. Colorimetric methods are based on a very simple principle which the following example may serve to illustrate.

When ammonium thiocyanate is added to a solution of a ferric salt, a red coloration is produced. The colour is perceptible when the solution contains even less than 1 part of iron in 10,000,000 (0.1 mgrm. per litre), and becomes more intense as the quantity of iron is increased. The amount of iron present can be ascertained by finding how much of a very dilute standard solution of a ferric salt must be added to a known quantity of water in order to produce, with ammonium thiocyanate, a coloration of equal intensity.

A colorimetric determination occupies but a few minutes, whereas gravimetric or volumetric methods, if applicable at all, would prove extremely tedious and probably less accurate. Colorimetric methods in general are suitable for the determination of small quantities only. Unless the total amount of substance present is known to be small, the solution containing it should be diluted to a known volume and a suitable portion taken for the analysis.

In colorimetric determinations it is usually essential (1) that the solutions to be compared contain as far as possible the same quantities of admixed substances (*e.g.* acid), (2) that they are at the same temperature, and (3) that they are diluted to the same volume before adding the reagent; otherwise serious errors may arise.

A number of examples of the application of colorimetric methods will be found in Part VIII. (Water Analysis).

Colorimeters.—Special instruments, known as colorimeters, are used for comparing the intensities of the colours of solutions. A simple form of colorimeter is shown in Fig. 57.¹

It consists essentially of two glass reservoirs and a darkened box. The glasses, G, are about 10 cm. high and 3 to 4 cm. square or rectangular section. Two opposite sides of each must be parallel, and the distances between

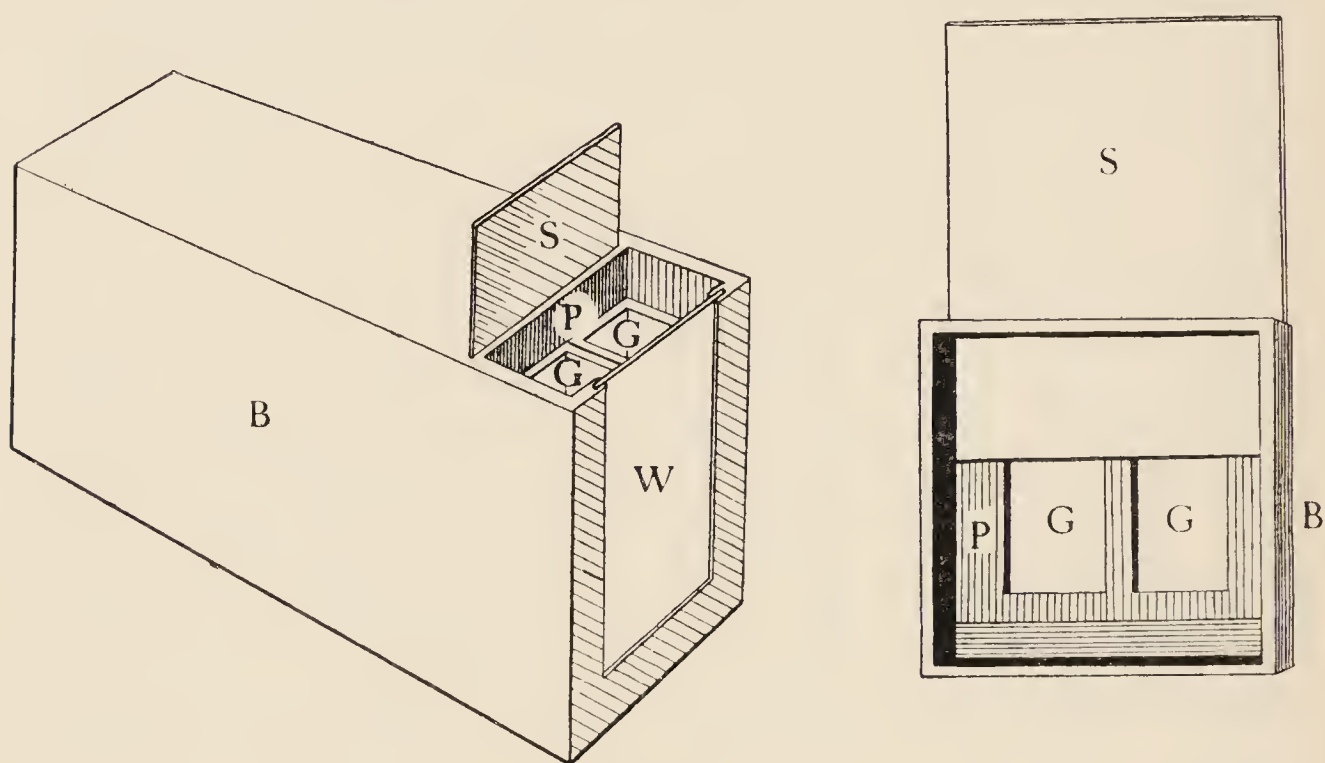


FIG. 57.

these sides must be identical (within 1 per cent.) in the two glasses. The other two sides of each should be blackened externally.

The glasses may be made from two rectangular specimen jars of the appropriate dimensions. Two opposite sides of each are ground off until it is found that the ground edges are parallel and the same distance apart in each case. Glass plates are then cemented on with Canada balsam or other material that will resist the action of dilute acid.

In order to exclude side light, the glasses are placed in

¹ This form of colorimeter is used by the United States Geological Survey, and is described in Hillebrand's *Analysis of Silicate and Carbonate Rocks*.

a box, B. The box measures about 30 cm. \times 10 cm. \times 10 cm. One end is closed by a piece of ground glass, W, the other end being open. About 5 cm. of the top of the box (next the ground glass) is removed to allow the insertion of the glasses. A thin wooden partition, P, provided with openings slightly narrower than the glasses, is inserted immediately behind the latter. Alongside the partition, a cardboard shutter, S, slides stiffly so as to remain at any desired height, in order to cut off all light except that which comes through the solutions in the glasses. The box and partitions are stained dead black inside and out.

The colorimeter is used in the following manner:—The solution to be tested is placed in one of the glasses, and in the other a known amount of the standard solution which is purposely made of a more intense colour than the unknown solution. Water from a burette is then cautiously added to the standard solution which is mixed by gentle stirring until the colours of the two solutions appear of equal intensity. The concentrations of the two solutions are then identical. When making the colour comparison, the box is held in the hand toward a well-lighted window.

If a colorimeter is not available, the colour comparison may be made with fair accuracy in cylinders of colourless glass (Nessler tubes). These tubes are usually graduated to contain 50 c.c. or 100 c.c., and the graduation mark must be at the same level in all tubes of equal capacity. In order to exclude side light, it is worth while providing the tubes with opaque covers open at the ends and made from stout brown paper. A glass tube on which a flattened bulb of appropriate size is blown (Fig. 58) should be provided for mixing the solutions in the tubes. The colour intensities are compared by holding the tubes close together over a white surface (*e.g.* a sheet of opal glass) and looking down into the tubes.

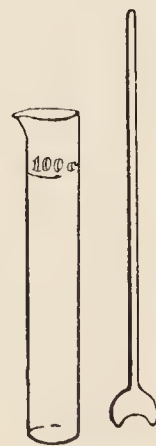


FIG. 58.

The general method of procedure is fully described in the first example given on the next page.

Iron.

A convenient method for the colorimetric determination of iron is based, as already stated, on the red coloration which ammonium thiocyanate gives with a solution of a ferric salt. The solution containing the iron must be acid, and a large excess of the thiocyanate must be used. The red coloration fades slowly on account of the spontaneous decomposition of the ferric thiocyanate.

The following solutions are required:—

(1) *Standard Iron Solution*.—Dissolve 0.864 gram of ammonium ferric sulphate in water, add 10 c.c. of dilute hydrochloric acid, and dilute to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of iron.¹

(2) *Ammonium Thiocyanate Solution*.—Dissolve 50 grams of the pure salt in 100 c.c. of water.

Procedure.—The iron must be present as a ferric salt. If the solution contains more than 0.3 mgrm. of iron, dilute it to a known volume.

Measure into a 100 c.c. Nessler tube a portion of the solution containing from 0.1 to 0.3 mgrm. of iron. (A preliminary trial may have to be made with a small portion.) Add 1 c.c. of concentrated hydrochloric acid (free from iron) and dilute to the graduation mark. Then add 5 c.c. of the ammonium thiocyanate solution, and mix. If the resulting coloration is very intense, use a smaller quantity of the iron solution.

Prepare four standard tints as follows:—Measure with a burette 0.5, 1, 2, and 3 c.c. of the standard iron solution into four 100 c.c. tubes, add 1 c.c. of concentrated hydrochloric acid to each, dilute to the mark, add 5 c.c. of the thiocyanate, and mix.

Compare the intensity of the colour given by the unknown solution with the standard tints. The comparison is made by holding the tubes close together over a white surface (e.g. a sheet of opal glass) and looking down into the tubes. It is unlikely that the colour will match any of the standards exactly, but is now easy to estimate, and then by actual trial to ascertain, what volume of the standard iron solution must be used to give a coloration of the same intensity.

¹ A more dilute standard solution, containing 0.173 gram of the iron alum per litre, may be found more convenient. One c.c. of this solution corresponds to 0.02 mgrm. of iron.

To most observers the solution in the tube held in the left hand appears slightly darker in colour than that in the right, even when the two tubes are filled with portions of the *same* solution. It is a good plan, therefore, in colorimetric comparisons generally, to interchange the tubes, and if the left-hand tube always appears the darker, it is certain that the intensities of the colorations are equal.

The following method of matching may also be used:— Suppose, for example, that the unknown solution gives a coloration that is a little more intense than a standard containing 1 c.c. of the iron solution. Transfer the unknown solution (its volume is 105 c.c.) to a measuring cylinder; then pour it gradually back into the Nessler tube until the colour (as viewed from above) matches that of the standard. If 95 c.c. is required, the iron in the portion of solution taken is equal to that contained in $1 \times \frac{105}{95} = 1.1$ c.c. of the standard iron solution, *i.e.* 0.11 mgrm.

If the quantity of iron taken requires more than about 3 c.c. of the standard solution to equal it, the colour is too deep for accurate comparison.

The colour comparison may be made more rapidly in the colorimeter as follows:—Measure into a 100 c.c. graduated flask a portion of the solution containing about 0.5 mgrm. of iron. Add 1 c.c. of concentrated hydrochloric acid and 5 c.c. of ammonium thiocyanate, and dilute to the graduation mark. In another 100 c.c. flask, prepare a standard solution of ferric thiocyanate containing 1 mgrm. or more of iron. Transfer the lighter coloured solution to one of the glasses of the colorimeter. Place a measured portion (10 c.c. to 20 c.c.) of the darker standard solution in the other glass and add water from a burette until the colours are of equal intensity, as described on p. 191.

Exercise.—Determine the amount of ferric salt in a sample of commercial ferrous sulphate or ferrous ammonium sulphate. Dissolve a weighed quantity (2 to 5 grams) in water to which 10 c.c. of dilute sulphuric acid has previously been added and dilute the solution to 250 c.c. Ascertain by trial how much of the solution must be diluted to 100 c.c. in order to give, with ammonium thiocyanate, a coloration of suitable intensity for comparison.

Titanium.

Hydrogen peroxide produces with an acid solution of titanium sulphate a strong yellow colour, the intensity of which with small amounts of titanium is proportional to the amount of titanium present. The colorimetric method based on this reaction is superior to all others for the determination of a small amount of titanium such as that commonly present in silicate rocks or iron ores.

The titanium sulphate solution must contain at least 5 per cent. of sulphuric acid. A mere trace of hydrofluoric acid in either the hydrogen peroxide or the titanium solution renders the results inaccurate. The error introduced by the presence of ferric sulphate, in consequence of its yellow colour, is negligible unless the original substance contains more than 5 per cent. of iron. If necessary, a correction may be applied, as indicated below.

The following solutions are required:—

(1) *Standard Titanium Solution*.—Weigh accurately in a platinum crucible 0.7500 gram of pure, dry potassium titanium fluoride, K_2TiF_6 . Add concentrated sulphuric acid and evaporate (Fig. 13, p. 24) almost to dryness. Repeat this operation several times until the hydrofluoric acid is completely expelled. Dissolve in a little sulphuric acid and dilute with 5 per cent. sulphuric acid to 250 c.c. One c.c. of the solution corresponds to 1.0 mgrm. TiO_2 .

(2) *Hydrogen Peroxide*.—A 3 per cent. ("ten volumes") solution, free from hydrofluoric acid.

(3) *Dilute Sulphuric Acid (5 per cent.)*.—Dilute 30 c.c. of concentrated sulphuric acid to 1 litre.

Procedure.—Dilute the titanium solution to a known volume. Transfer a measured portion containing from 2 to 5 mgrms. of TiO_2 to a 100 c.c. graduated flask, add 5 c.c. of hydrogen peroxide, and dilute with 5 per cent. sulphuric acid to the graduation mark. Measure 10 c.c. of the standard titanium solution (corresponding to 10 mgrms. TiO_2) into another 100 c.c. flask, add 5 c.c. of hydrogen peroxide, and dilute with 5 per cent. sulphuric acid to the mark.

Transfer the lighter coloured solution to one of the glasses of the colorimeter. Place a measured portion (10 c.c.

to 20 c.c.) of the darker standard solution in the other glass and add water from a burette until the colours are of equal intensity, as described on p. 191.

If the original solution contains ferric sulphate, the requisite amount of iron alum must be added to the standard in order to compensate for the yellow colour of the ferric salt.

Determination of Titanium in Iron Ore.—Weigh accurately in a platinum crucible about 0.5 gram of the finely powdered ore, and fuse it with about 5 grams of dry sodium carbonate as described in detail on p. 253. When the fusion is complete, allow the crucible to become cold and then place it upright in a covered beaker containing 50 c.c. of dilute sulphuric acid. Upset the crucible with a glass rod and warm gently until the mass is completely detached from the crucible. Remove the crucible and rinse it. Add 3 c.c. of concentrated sulphuric acid and heat until all that is soluble has dissolved. Filter into a 100 c.c. graduated flask. After cooling, add 5 c.c. of hydrogen peroxide and dilute to the mark.

Determine the titanium in the solution colorimetrically. To correct for the colour of the ferric sulphate, first make a rough determination in order to ascertain the approximate volume of the standard after dilution, and then repeat the determination after adding the requisite amount of iron alum to a fresh portion of the standard.

Copper.

When potassium ferrocyanide is added to a very dilute solution of a copper salt, a purple-brown coloration is produced. The test is more delicate if the solution contains a large quantity of some neutral salt, such as ammonium nitrate. One part of copper in about 2,000,000 parts of water can be detected. The presence of iron interferes with the test, but lead, unless present in large quantity, does not. The following solutions are required:—

(1) *Standard Copper Solution.*—Dissolve 0.393 gram of pure copper sulphate in water and dilute the solution to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of copper.

(2) *Potassium Ferrocyanide Solution*.—Dissolve 1 gram in 100 c.c. of water.

(3) *Ammonium Nitrate Solution*.—Dissolve 10 grams in 100 c.c. of water.

Procedure.—The solution containing the copper must be neutral. If iron is present it must be removed as follows:—Add 1 c.c. of concentrated nitric acid and evaporate to a small volume. Precipitate the iron by adding a slight excess of ammonia, filter, and wash. Dissolve the ferric hydroxide in dilute nitric acid, reprecipitate with ammonia, filter, and wash. Combine the two filtrates, boil until free from ammonia, cool, and dilute to a known volume.

Measure a suitable portion of the solution (corresponding to about 0.5 mgrm. of copper) into a 100 c.c. Nessler tube, add 5 c.c. of the ammonium nitrate solution, and dilute to the mark. Then add 1 c.c. of the potassium ferrocyanide solution, and mix. If the coloration is not of a suitable intensity for accurate comparison, a larger or a smaller quantity of the copper solution should be taken. Then find by trial, as described in the case of iron, how much of the standard copper solution is required to give, under the same conditions, a coloration of equal intensity.

Copper may be determined colorimetrically in presence of iron by means of hydrogen sulphide, as described under lead, provided that lead and other metals forming sulphides insoluble in acid are absent.

Ammonia.

It is sometimes necessary to determine with accuracy a very much smaller quantity of ammonia than can be dealt with by the ordinary volumetric method. In drinking water, for example, 1 part of ammonia in 20,000,000 (0.05 mgrm. per litre) is of importance from a hygienic standpoint. The detection and quantitative determination of a trace of ammonia so minute is possible by means of Nessler's reagent. This reagent is a mixture of potassium mercuric iodide (K_2HgI_4) and sodium or potassium hydroxide, and it gives a brownish-yellow coloration with extremely dilute ammonia solutions. On account of the delicacy of the test (one part in 100,000,000 is easily detected), and of the small

amounts of ammonia usually dealt with, the colorimetric determination of ammonia must be carried out in a room that contains no ammonia or ammonium salts, and not in the general laboratory.

The following materials are required:—

(1) *Nessler Solution*.—Dissolve (a) 35 grams of potassium iodide in 150 c.c. of water; (b) 17 grams of mercuric chloride in 300 c.c. of water; and (c) 120 grams of sodium hydroxide in 300 c.c. of water. Add (b) to (a) gradually, while shaking, until a slight red precipitate remains permanent; then add (c) and dilute the mixture to 1 litre. Finally, add a little of the mercuric chloride solution until a slight permanent turbidity again forms. Set the mixture aside until clear, and then decant into a bottle fitted with a rubber stopper.

Transfer a portion of the solution to a small bottle for immediate use (Fig. 27 on p. 55). The pipette for measuring the solution is graduated to deliver about 2 c.c. In order that the slight sediment that is sometimes present may not be disturbed, the pipette should not reach to the bottom of the bottle.

(2) *Standard Ammonium Chloride Solution*.—Dissolve 3.14 grams of pure ammonium chloride in water and dilute the solution to 1 litre. As required, dilute 10 c.c. of this solution to 1 litre. One c.c. of the dilute solution corresponds to 0.01 mgrm. of ammonia.

(3) *Ammonia-free Water*.—Ordinary distilled water frequently contains a trace of ammonia. In order to ascertain if this is the case, mix 50 c.c. of the water with 2 c.c. of Nessler solution. If no yellow coloration develops within three minutes, the water is fit for use. As a rule, it is necessary to prepare ammonia-free water in the following way:—

Add about 1 gram of recently ignited sodium carbonate crystals to about 2 litres of distilled water contained in a large flask or copper boiler. Distil the water and test 50 c.c. of the distillate from time to time with Nessler solution. As soon as it ceases to give a coloration, collect the water in a clean Winchester. (Stop the distillation when the volume of water in the flask is reduced to about 250 c.c.) Keep the Winchester stoppered and away from sources of ammonia.

Procedure.—If the solution to be examined contains more than 1 mgrm. of ammonia per litre, dilute it to a known volume with ammonia-free water. If it contains less than 0.2 mgrm. per litre, or if any salts that form insoluble hydroxides are present, distil the solution with a little sodium carbonate; all the ammonia is thus obtained in the first portion of the distillate (*cf.* “Water Analysis,” p. 341).

Measure into a 50 c.c. Nessler tube a portion of the solution containing not more than 0.1 mgrm. of ammonia, and dilute it to the mark with ammonia-free water. Add 2 c.c. of Nessler solution and mix with the stirring-bulb. (The stirring-bulb must not be laid on the bench but should be kept in a beaker containing distilled water.) Then ascertain, by trial, how much of the standard ammonium chloride solution must be diluted to 50 c.c. (with ammonia-free water) to give a coloration of equal intensity. The full intensity of the colour is not obtained immediately the reagent is added, and an interval of three minutes should elapse before the solutions are compared.

Notes.—The Nessler solution must always be added to the solution containing ammonia, not *vice versa*. If the solution contains more than 0.1 mgrm. of ammonia in 50 c.c., the coloration is too intense for accurate comparison. The coloration given by 2 to 3 c.c. of the standard ammonium chloride solution is the most suitable.

Lead.

The most satisfactory method for the determination of a minute quantity of lead depends on the coloration produced when hydrogen sulphide is added to the solution containing it. The solution should be slightly acid—preferably with acetic acid. Copper and other metals that form sulphides insoluble in acid interfere, but dilute solutions of iron salts give no coloration with hydrogen sulphide in presence of acid.

The following solutions are required:—

(1) *Standard Lead Solution.*—Dissolve 0.1830 gram of lead acetate in water, add acetic acid until a clear solution is obtained, and dilute to 1 litre. One c.c. of the solution corresponds to 0.1 mgrm. of lead.

(2) *Hydrogen Sulphide Solution*.—Saturate some freshly boiled (and cooled) distilled water with the gas, transfer the solution to a burette, and cover it with about 1 c.c. of olive oil. Protected in this way from the air, the solution will remain clear for a long time, especially if kept in the dark.

Procedure.—If the solution to be tested is strongly acid, neutralise the excess of acid with sodium hydroxide and then add a little sodium acetate. If it contains more than 0.5 mgrm. of lead, dilute it to a known volume.

Measure into a 100 c.c. Nessler tube a portion of the solution containing from 0.1 to 0.5 mgrm. of lead, add 2 c.c. of acetic acid, and dilute to 100 c.c. Then add 2 c.c. of hydrogen sulphide solution and mix gently. (Vigorous agitation may cause precipitation of the lead sulphide. In order to prevent precipitation, 10 c.c. of a concentrated solution of sugar may be mixed with the solution before adding hydrogen sulphide.)

Then find, by trial, how much of the standard lead solution is required to give, under the same conditions, a coloration of equal intensity. The coloration gradually fades if it is exposed to full daylight.

Manganese.

The gravimetric determination of a small amount of manganese in a complex substance is seldom accurate, largely owing to the difficulty of completely separating it from the other constituents of the substance. As a rule it is possible to determine the manganese in a separate portion of the substance by a colorimetric method.

The method depends on the conversion of the manganese into permanganic acid by means of ammonium persulphate in presence of a small quantity of silver nitrate. (If no silver salt is present, the manganese is precipitated as manganese dioxide.) The solution in which the manganese is to be determined must contain nitric acid or sulphuric acid, but no chloride.

The following solutions are required:—

(1) *Standard Manganese Solution*.—Dissolve 0.144 gram of pure potassium permanganate in about 100 c.c. of water

and pass a current of sulphur dioxide through the solution until it becomes clear and colourless. Boil the solution until free from sulphur dioxide, cool, and dilute to 1 litre. One c.c. of the solution corresponds to 0.05 mgrm. of manganese.

(2) *Silver Nitrate Solution*.—Dissolve 1 gram of silver nitrate in 500 c.c. of water.

Procedure.—If the solution contains more than 1 mgrm. of manganese, dilute it to a known volume; if it contains less than 1 mgrm., evaporate the solution to about 50 c.c.

Transfer the solution, or a measured portion of it, containing about 1 mgrm. of manganese, to a small flask, add 5 c.c. of concentrated nitric acid, and 10 c.c. of the silver nitrate solution. (If a trace of chloride is present and a turbidity appears, shake vigorously to coagulate the silver chloride and filter into another flask.) Then add 1 gram of ammonium persulphate and warm the flask on the steam-bath until the pink colour appears. After about a minute, remove the flask. When the colour has fully developed, cool the solution by placing the flask in cold water. Dilute the solution to 100 c.c. in a standard flask.

Measure into another flask a portion of the standard manganese solution containing somewhat more manganese than is present in the unknown solution. Add 5 c.c. of concentrated nitric acid, oxidise with silver nitrate (10 c.c. for every mgrm. of manganese) and ammonium persulphate, and dilute to 100 c.c. in a standard flask.

Transfer the lighter coloured solution to one of the glasses of the colorimeter. Place a measured portion (10 c.c. to 20 c.c.) of the darker standard solution in the other glass and add water from a burette until the colours are of equal intensity, as described on p. 191.

Exercise.—Determine the percentage of manganese in a sample of commercial lime. Before commencing the determination, make a rough experiment, using about 1 gram of the lime, in order to ascertain approximately how much manganese is present. Dissolve the lime in nitric acid.

Determination of Manganese in Steel.—Weigh accurately 0.2 gram of the sample of steel (in the form of clean drillings) and of a standard steel in which the percentage of manganese is known. Place the weighed portions in small

flasks. Add to each flask 10 c.c. of a mixture of concentrated nitric acid and water in equal volumes, and warm the flasks on the steam-bath until the steel has dissolved and all oxides of nitrogen are driven off. Add 10 c.c. of the silver nitrate solution and then 1 gram of ammonium persulphate, and warm the flasks on the steam-bath until the oxidation commences. Remove the flasks from the steam-bath and, after the colour has fully developed, cool the solutions, transfer them to 100 c.c. standard flasks, and dilute to the graduation marks.

Measure 10 c.c. of the standard steel solution into an Eggertz "carbon" tube,¹ and dilute to some convenient volume, *e.g.* 15 or 20 c.c. Into another similar tube measure 10 c.c. of the solution of the sample. (If the standard solution is darker in colour than that of the sample, the standard must be further diluted, or another standard containing less manganese must be prepared.)

Then add water, little by little, to the tube containing the sample, mixing thoroughly after each addition of water, until the colour matches that of the standard solution. The solutions are compared by placing the tubes in a colorimeter box similar to that described on p. 190, so as to exclude all light except that which passes through the solutions; or instead of using "carbon" tubes, the solutions may be compared in the colorimeter as described on p. 191.

If the steel contains more than 0.75 per cent. of manganese, use only 0.1 gram.

Example.—A standard steel contained 0.3 per cent. of manganese, and it was diluted in the graduated tube to 15 c.c.—each cubic centimetre then corresponded to 0.02 per cent. The volume of the solution of the sample when the colours matched was 20 c.c.; the percentage of manganese in the sample was therefore $20 \times 0.02 = 0.4$ per cent.

Nickel.

Very minute quantities of nickel may be determined by means of a solution of diacetyldioxime which produces a scarlet precipitate with nickel salts (see p. 240) and gives an

¹ Tubes of equal bore (about 1 cm.), closed at one end and graduated like a burette; used for the colorimetric determination of carbon in steel.

immediate pink coloration with 0.01 mgrm. of nickel in 5 c.c. of solution. A trace of iron (ferric) does not interfere. The following solutions are required:—

(1) *Standard Nickel Solution*.—Dissolve 0.673 gram of nickel ammonium sulphate in water and dilute the solution to 1 litre. As required, dilute 10 c.c. of this solution to 100 c.c. One c.c. of the dilute solution contains 0.01 mgrm. of nickel.

(2) *Diacetyldioxime (Dimethylglyoxime) Solution*.—Dissolve 1 gram in 100 c.c. of absolute alcohol.

Procedure.—The nickel solution must be neutral or very faintly acid, and should contain no nitrate. Dilute it to a known volume so that 100 c.c. contains about 1 mgrm. of nickel. Place a measured portion containing from 0.01 to 0.1 mgrm. of nickel in a small Nessler tube. Add 0.5 c.c. of dilute ammonia and 0.5 c.c. of diacetyldioxime solution. Mix by gentle stirring and allow the colour to develop during two minutes. Dilute to 25 c.c. Then find, by trial, how much of the standard nickel solution is required to give, under similar conditions, a coloration of equal intensity. The insoluble nickel salt may separate as a red precipitate after a time, and the colour comparison should therefore be made as quickly as possible.

PART V

SYSTEMATIC QUANTITATIVE ANALYSIS

ALUMINIUM.

NEITHER a volumetric nor an electrolytic method is available for the determination of aluminium.

In the analysis of a complex mixture, iron and aluminium are separated from all other metals before separation from one another, and are obtained finally as a mixture of ferric oxide and alumina. The iron in the mixed oxides may be determined volumetrically and the aluminium found by difference.

Forms in which Aluminium is precipitated.

Aluminium Hydroxide.—This is the easiest method for the determination of aluminium, but is limited in applicability on account of the general insolubility of metallic hydroxides. For details of the procedure, see p. 163.

Basic Aluminium Acetate.—The method serves to separate aluminium (and iron) from nickel, cobalt, manganese, zinc, calcium, and magnesium.

Aluminium Phosphate.—This method is of special value for the separation of aluminium and iron.

Determination of Aluminium (and Iron) by the Basic Acetate Method.

OUTLINE OF METHOD.—The solution is neutralised and largely diluted. Ammonium acetate is added and the solution boiled, whereby basic aluminium and ferric acetates are precipitated. After a second precipitation by ammonia, the precipitate is ignited and the mixture of Fe_2O_3 and Al_2O_3 is weighed. The Fe_2O_3 in the mixed oxides is then determined and the Al_2O_3 found by difference.

Basic Aluminium Acetate is a bulky, gelatinous precipitate, insoluble in water or in slightly alkaline solutions.

It probably varies considerably in composition according to the method of preparation. Unless precipitated under the exact conditions given below, it forms a jelly-like mass which cannot be filtered. It is readily soluble in all acids. It occludes to some extent all soluble salts that may be present in the solution, and these cannot be completely removed by washing. If washed with water, it becomes more gelatinous and chokes the pores of the filter.

On ignition it is completely converted into Al_2O_3 , but if the solution contained alkali salts, the precipitated basic acetate is contaminated with occluded alkali salts, and the oxide obtained is also impure.

Basic Ferric Acetate corresponds closely in properties with the aluminium salt, but is less soluble in acetic acid.

Procedure.—The basic acetate method is never used unless it is necessary to separate iron and aluminium from other metals. In the following description of the method it is therefore assumed that a separation of iron and aluminium from other metals, such as manganese, is desired.

Introduce the solution, which should contain no sulphate, into a beaker of at least 750 c.c. capacity, and to the cold solution add ammonia cautiously, with constant stirring, until a slight *permanent* precipitate is produced. Then add dilute hydrochloric acid, drop by drop, stirring for about a minute after each drop, until the precipitate is just redissolved. Unless the amount of iron is small, the solution at this stage should be clear brown in colour—if it is yellow, too much acid has been added. Add 3 grams of ammonium acetate dissolved in a little water. If the conditions have been correctly observed, no precipitate will form at this stage, but the solution will become darker and redder in colour. Dilute with hot water to about 400 c.c. and heat until boiling. *Boil for one or two minutes only, and then filter as quickly as possible through an 11-cm. paper, using slight suction.* (If the solution is boiled for more than two minutes, or is allowed to cool before filtration, the precipitate becomes so gelatinous that filtration is almost impossible.)

The precipitate is mainly basic ferric and aluminium acetates, but contains also occluded salts. Wash twice with hot water and then redissolve the precipitate by pouring hot

dilute nitric acid on it without removal from the filter paper. Wash the paper once with hot dilute nitric acid and then with hot water. Add 2 c.c. of concentrated nitric acid to the solution, and reprecipitate with a slight excess of ammonia. Heat until boiling, filter, and wash thoroughly with hot water. (Combine the two filtrates for the determination of manganese, etc.)

Incinerate the filter paper together with the precipitate in a platinum crucible without previous drying, ignite over a Méker burner, and weigh the mixture of ferric oxide and alumina.

Separate Determination of the Iron and Aluminium.—Fuse the mixed oxides with potassium pyrosulphate (p. 287), determine the iron volumetrically, and calculate the weight of ferric oxide equivalent to it. The difference between this and the weight of the mixed oxides is the weight of the alumina.

Determination of Aluminium as Aluminium Phosphate.

OUTLINE OF METHOD.—The aluminium is precipitated in presence of acetic acid by boiling the solution with sodium phosphate and sodium thiosulphate. The precipitate is ignited, and is weighed as AlPO_4 .

Procedure.—To the acid solution (which should not contain more than 50 mgrms. of aluminium, and may also contain iron), add about 2 grams of sodium phosphate, and then ammonium carbonate until a permanent precipitate is obtained. Redissolve the precipitate in dilute hydrochloric acid and add 1 c.c. in excess. Dilute the solution to about 300 c.c., add about 5 grams of sodium thiosulphate, heat until boiling, and add 20 c.c. of acetic acid. Boil for twenty minutes in order to coagulate the precipitated sulphur and to reduce the iron to the ferrous condition. (Ferrous phosphate is not precipitated in presence of acetic acid.)

Filter, and wash with hot water. Dry the precipitate (partially at least) and incinerate the filter together with the precipitate. Ignite and weigh the aluminium phosphate obtained.

AMMONIUM.

Ammonia, whether as free ammonia or as an ammonium salt, is determined volumetrically. For details, see p. 72.

A colorimetric method for the determination of traces of ammonia is described on page 196.

ANTIMONY.

On account of their comparative simplicity and greater accuracy, volumetric methods for the determination of antimony (see pp. 89, 117, and 139) are preferable to any gravimetric method. The bromate method (p. 139) is applicable to mixtures containing antimony, tin, and arsenic.

The gravimetric determination of antimony is a matter of some difficulty, since in ordinary practice the problem involves the separation of antimony from other elements such as arsenic, with similar chemical properties.

In the analysis of a complex mixture, antimony is usually precipitated as sulphide, together with other metals of the copper and arsenic group.

Antimony Sulphide.—From a hot solution of an antimonious salt, hydrogen sulphide precipitates an orange precipitate of antimonious sulphide which is often contaminated with pentasulphide or with free sulphur.

Antimony sulphide is readily soluble in alkali hydroxides or sulphides, and in ammonium sulphide. The solubility is inappreciable in cold hydrochloric or sulphuric acid (saturated with hydrogen sulphide) up to about 4N solution. No antimony is precipitated by hydrogen sulphide from a 7N hydrochloric acid solution, and a complete separation from arsenic may be obtained by precipitating the arsenic from a strongly acid solution (two-thirds concentrated hydrochloric acid, by volume) to which about 3 grams of tartaric acid have been added. The arsenic sulphide is filtered and washed with hydrochloric acid (2 : 1). The antimony sulphide is then precipitated by diluting the filtrate with double its volume of warm water and again saturating with hydrogen sulphide. The precipitate is allowed to settle; the supernatant liquid is filtered through a hardened paper, and the precipitate is washed by decantation with dilute acetic acid containing hydrogen sulphide. The filter paper is then

opened out on the convex side of a clock-glass, and the sulphide is rinsed from it into the beaker containing the main part of the precipitate with hydrochloric acid (2 : 1) in which some potassium chlorate has been dissolved. The contents of the beaker are heated until the precipitate has dissolved, and, after expelling chlorine, the antimony is determined volumetrically.

ARSENIC.

Arsenic may be determined volumetrically as described on pp. 116 and 139.

Forms in which Arsenic is precipitated.

Arsenic Sulphide.—This method gives accurate results if all the arsenic is in the pentavalent state. The solution, cooled in ice, should be slowly diluted with twice its volume of concentrated hydrochloric acid and saturated with hydrogen sulphide. After filtration through a Gooch crucible, the precipitate should be washed with water, dried at 105° to 110° , and weighed as As_2S_5 .

Magnesium Ammonium Arsenate.—The arsenic must be present as arsenate.

Determination as Magnesium Ammonium Arsenate.

OUTLINE OF METHOD.—The arsenic is precipitated by “magnesia mixture” in presence of a large excess of ammonia, dried at 110° , and weighed as $\text{MgNH}_4\text{AsO}_4$.

Magnesium Ammonium Arsenate is a white, crystalline precipitate, slightly soluble in water and somewhat less soluble in ammonia solution. The precipitated salt contains six molecules of water of crystallisation, and cannot be completely dehydrated at 100° . At 110° , it quickly becomes anhydrous, and at somewhat higher temperatures begins to decompose. On ignition, it is converted into magnesium pyroarsenate which, however, decomposes slightly and loses weight if the temperature is very high.

The following solution is required for the precipitation :—

Magnesia Mixture.—Dissolve 6 grams of magnesium chloride and 7 grams of ammonium chloride in water, add 10 c.c. of concentrated ammonia, and dilute to 100 c.c.

Procedure.—Evaporate the arsenate solution to 100 c.c. and add 1 gram of ammonium chloride. Run in, drop by drop, 20 c.c. of magnesia mixture, stirring briskly, but without touching the beaker with the stirring-rod. Then add 15 c.c. of concentrated ammonia and set aside for twelve hours. Decant through a Gooch crucible, and bring the precipitate into the crucible with the help of the filtrate. Wash the precipitate with a dilute solution of ammonia (25 c.c. of 2N ammonia diluted to 100 c.c.) until the filtrate is free from chloride. Avoid over-washing, as the precipitate is sparingly soluble in dilute ammonia. Place the crucible in the air-oven and raise the temperature slowly, drying finally at 110° to 115° until of constant weight.

BARIUM.

Forms in which Barium is precipitated.

Barium Sulphate.—This is the usual method, and serves for the separation of barium from almost all other metals.

Barium Chromate.—This method is also convenient and accurate. Barium may be separated from strontium by precipitation as chromate from a solution acidified with acetic acid.

Determination of Barium as Sulphate.

The solution is made slightly acid with hydrochloric acid, heated until boiling, and the barium precipitated by a hot dilute solution of sulphuric acid. In all other respects the procedure is identical with that adopted for the determination of sulphate (see p. 169).

Determination of Barium as Chromate.

OUTLINE OF METHOD.—The barium is precipitated from neutral or slightly acid solution by ammonium chromate. The barium chromate is filtered through a Gooch crucible, washed with hot water, dried, and weighed as BaCrO_4 .

Barium Chromate is a yellow, finely divided precipitate which is very slightly soluble in water. At 18° , 1 litre of water dissolves about 4 mgrms., and the solubility is greater at higher temperatures. It is much less soluble in a dilute ammonium chromate solution. It is appreciably soluble in

dilute acetic acid and readily soluble in mineral acids. It can be dried completely at 100° , and may be heated to a red heat without decomposition. Heated with organic matter, partial reduction occurs with formation of green chromic oxide; on further ignition with free access of air this is reconverted into chromate.

Procedure.—Neutralise the solution with ammonia or hydrochloric acid, add 1 c.c. of acetic acid, and dilute to about 150 c.c. Heat the solution until boiling, and precipitate the barium with a hot, dilute solution of ammonium chromate.¹ Place the beaker on the steam-bath until the precipitate settles. Allow to cool. Filter through a Gooch crucible. Rinse the beaker and transfer the precipitate to the crucible with a dilute (0.2 per cent.) solution of ammonium chromate. Wash finally with cold water until the filtrate is free from chromate. (The precipitate is very often finely divided and is apt to run through the filter.)

Place the Gooch crucible inside a nickel crucible and heat with a small flame until the precipitate has a uniform yellow colour. Weigh the BaCrO_4 obtained.

BISMUTH.

In the preparation of a solution for analysis it is advisable, if possible, to use nitric acid in preference to hydrochloric or sulphuric acid, in order to simplify the subsequent analysis. In the case of a complex ore or alloy, it is immaterial which acid is used, because it is usually necessary to precipitate the copper and arsenic groups together as sulphides, and afterwards to separate these by appropriate methods.

Electrolytic methods for the determination of bismuth have been proposed but cannot be recommended.

Forms in which Bismuth is precipitated.

Bismuth Sulphide.—Bismuth may be precipitated as sulphide together with other members of the copper and arsenic groups. If the bismuth sulphide is to be weighed as

¹ Dissolve 1.25 gram of ammonium dichromate (free from sulphate) in 100 c.c. of water and add sufficient dilute ammonia—about 5 c.c.—to give a lemon-yellow coloured solution.

such, it is desirable to precipitate in presence of sulphuric (not hydrochloric) acid.

Basic Bismuth Carbonate.—This method is applicable in presence of sodium, potassium, and ammonium salts only. The results are inaccurate if the solution contains sulphate or chloride.

Metallic Bismuth.—This method is available in presence of zinc, aluminium, sodium, potassium, and ammonium salts.

Basic Bismuth Nitrate.—This method may be used to separate bismuth from all other metals except tin, antimony, and mercury.

Determination of Bismuth as Basic Carbonate.

OUTLINE OF METHOD.—The bismuth is precipitated by ammonium carbonate as basic bismuth carbonate, which is converted into oxide by ignition and weighed as Bi_2O_3 .

Basic Bismuth Carbonate is a granular, white precipitate which is readily soluble in acids and slightly soluble in ammonia. If precipitated from a solution containing chloride or sulphate, it is always contaminated with basic chloride or sulphate. As these basic salts are not completely converted into oxide by ignition, the method is applicable only in absence of all salts other than nitrate.

Bismuth Oxide, Bi_2O_3 , is obtained when the basic nitrate or carbonate is ignited. Complete decomposition occurs on ignition at a low red heat. As the molten oxide attacks porcelain, it is inadvisable to heat above the temperature at which the oxide just melts. The oxide is readily reduced to metal by carbon, and the filter paper should therefore be completely incinerated before the precipitate is brought into the crucible.

Procedure.—Dilute the solution with water to about 50 c.c. (a slight turbidity may be produced on dilution). Add ammonium carbonate in slight excess and boil until most of the ammonia is expelled. Filter, wash the precipitate with hot water, and dry. Incinerate the filter-paper apart from the precipitate in a porcelain crucible, and oxidise any reduced oxide with nitric acid (compare p. 167). Transfer the main precipitate to the crucible and heat with a moderate flame—the heat being so regulated that the bismuth oxide is barely fused—and weigh as Bi_2O_3 .

Determination of Bismuth as Oxide after Precipitation as Metal.

OUTLINE OF METHOD.—The bismuth is precipitated as metal by formaldehyde and alkali. The precipitated metal, which is usually contaminated with alkali, is dissolved in dilute nitric acid and reprecipitated as carbonate. By ignition, the carbonate is converted into the oxide, Bi_2O_3 .

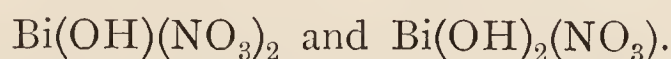
Metallic Bismuth, as obtained by precipitation, is a black, spongy powder which is insoluble in water or in alkaline solutions.

Procedure.—To the bismuth solution, add about 10 c.c. of 40 per cent. formaldehyde solution and excess of pure 10 per cent. sodium hydroxide solution. Warm on the steam-bath. When the precipitate has settled and the supernatant liquid has become clear, add a further 5 c.c. of formaldehyde and a few cubic centimetres of sodium hydroxide. Heat the solution until boiling, and press together with a glass rod the spongy precipitate of metal, in order to facilitate filtration. Filter, wash thoroughly with hot water, and then dissolve the precipitate with a little hot, dilute nitric acid. Wash the filter paper several times with hot, dilute nitric acid. Precipitate the bismuth as basic carbonate and convert to oxide, as described on the preceding page.

Determination of Bismuth as Basic Nitrate.

OUTLINE OF METHOD.—The bismuth is obtained in solution as nitrate, and is precipitated as the basic nitrate by large dilution and neutralisation. The basic nitrate is converted into oxide by ignition, and weighed as Bi_2O_3 .

Basic Bismuth Nitrate is usually a mixture of—



It is practically insoluble in cold water, and still less soluble in a very dilute solution of ammonium nitrate. It is readily soluble in acids unless extremely dilute; in the precipitation, however, the solution should still contain a trace of acid, otherwise other metals are precipitated with the bismuth. If precipitated from a solution containing more than a small amount of chloride, the precipitate is contaminated with bismuth oxychloride which is not completely converted into oxide by ignition.

Bismuth Oxide.—The properties of bismuth oxide are described on p. 210.

Procedure.—The bismuth solution must not contain more than a trace of chloride; if it contains chloride in quantity, add 5 c.c. of concentrated nitric acid and evaporate until of syrupy consistency; then add a further 5 c.c. of nitric acid and again concentrate the solution. After this treatment the solution will be practically free from chloride.

To the bismuth nitrate solution, contained in a 700-1000 c.c. beaker, add 500 c.c. of water and 5 c.c. of methyl orange solution. (Partial precipitation of the basic nitrate usually occurs on dilution.) Add ammonia drop by drop, with constant stirring, until the pink colour is almost, but not quite, discharged. Set the solution aside for one hour, and then filter. Wash with a dilute solution (2 grams per litre) of ammonium nitrate, dry at 100° , remove the precipitate as completely as possible from the paper, and incinerate the paper before addition of the precipitate (p. 153). The ignition of the precipitate should be carried out with the crucible covered, and with a very small flame at first, the temperature being raised slowly. If the heating is rapid, the gases given off during the decomposition of the nitrate carry away mechanically some of the solid. The final temperature should be barely sufficient to fuse the bismuth oxide.

BORATE.

Boric acid or the borate in alkali borates, such as borax, may be determined by the volumetric method described on p. 67.

Mineral borates, such as borocalcite or boracite, or alkali borates containing carbonate, are first decomposed by boiling with dilute hydrochloric acid under a reflux condenser. (The condenser is necessary in order to prevent loss of boric acid, which is volatile in steam.) The resulting solution is neutralised with sodium hydroxide using methyl orange as indicator, glycerol or mannitol is added, and the boric acid titrated as described on p. 67.

If appreciable quantities of iron and aluminium are present in the borate, this method of analysis leads to high

results, and it is difficult to remove the iron and aluminium without at the same time losing some boric oxide. In order to obtain accurate results in such cases, and also in the analysis of silicates containing boric oxide, a distillation method, depending on the formation of volatile methyl borate, must be used. For a description of this method, see Mellor, *Quantitative Inorganic Analysis*.

BROMIDE.

Bromide is most readily determined volumetrically (see pp. 125 and 129).

Bromide may also be determined gravimetrically by precipitation as silver bromide. The procedure is identical with that adopted for the determination of chloride (see p. 164).

Silver Bromide is less soluble than the chloride. One litre of water dissolves 0.1 mgrm. at 20° and 3.7 mgrms. at 100°. It is insoluble in nitric acid, sparingly soluble in ammonia, and appreciably soluble in concentrated solutions of most salts. It is darkened, with partial decomposition, by light, though to a less extent than the chloride. It melts at 422° and acquires a darker colour. It can be dried completely at 100°.

CADMIUM.

The separation of cadmium from certain metals, such as zinc, is a matter of some difficulty, and for methods of analysis applicable to complex ores or alloys, reference should be made to larger text-books. The analysis of Wood's alloy (tin, lead, cadmium, and bismuth) is described on p. 278.

Forms in which Cadmium is precipitated.

Metallic Cadmium (Electrolytic).—This is a convenient and accurate method. For details, see p. 186.

Cadmium Sulphate.—This method serves to separate cadmium from metals of the iron, zinc, and calcium groups. If other members of the copper group are present, further treatment is necessary.

Determination of Cadmium as Sulphate.

(After precipitation as Sulphide.)

OUTLINE OF METHOD.—The solution is acidified with sulphuric acid, and the cadmium is precipitated with hydrogen sulphide. The cadmium sulphide is dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, and the residue, CdSO_4 , is weighed.

Cadmium Sulphide is a yellow precipitate, insoluble in dilute acids or alkalis. It is readily soluble in concentrated hydrochloric acid. It may be completely precipitated by hydrogen sulphide from a solution that contains, in each 100 c.c., 10 to 12 c.c. of concentrated hydrochloric acid, or 5 to 7 c.c. of concentrated sulphuric acid; under these conditions very little zinc will be precipitated with the cadmium. The precipitate is always contaminated with compounds such as $\text{Cd}_2\text{Cl}_2\text{S}$ or $\text{Cd}_2\text{SO}_4\text{S}$, and must therefore be converted into cadmium sulphate before weighing.

Cadmium Sulphate is colourless. It may be heated to a temperature approaching redness without decomposition. At a higher temperature it is slowly converted into oxide, becoming first yellow and then dark brown.

Procedure.—To the cadmium solution, add 5 c.c. of concentrated sulphuric acid, dilute to 100 c.c., and saturate with hydrogen sulphide. Filter, and wash with 5 per cent. ammonium nitrate solution. Dissolve the precipitate in the minimum amount of concentrated hydrochloric acid, wash the filter with hot dilute acid, and transfer the filtrate and washings to a large crucible. Add 0.5 c.c. of concentrated sulphuric acid, and evaporate as far as possible on the steam-bath. Place the crucible inside a larger nickel crucible or an air-bath (Fig. 14, p. 25) and heat gently until no more fumes of sulphuric acid are given off. Weigh the CdSO_4 .

CALCIUM.

Calcium may be determined volumetrically by the method given on p. 85.

In gravimetric analysis, calcium is always determined by precipitation as oxalate, after removal of the copper, iron and zinc groups. (For details, see pp. 176 and 283.)

CARBONATE.

Carbonate may be determined either gravimetrically or volumetrically in various ways. Two gravimetric methods are in common use, viz.:—

1. A direct method, in which the carbon dioxide, expelled from the carbonate by the action of acid, is absorbed by soda-lime and weighed.

2. An indirect method, in which the loss of weight due to the escape of the carbon dioxide from an apparatus is ascertained.

Direct Method.

OUTLINE OF METHOD.—A weighed quantity of the substance is mixed with dilute acid in a small flask connected with a series of drying tubes, and with two absorption tubes containing soda-lime. The soda-lime tubes are weighed before and after the experiment.

The Apparatus (Fig. 59) consists of the following:—

A. A distilling flask, of about 125 c.c. capacity, provided with a rubber stopper and dropping funnel. The stem of

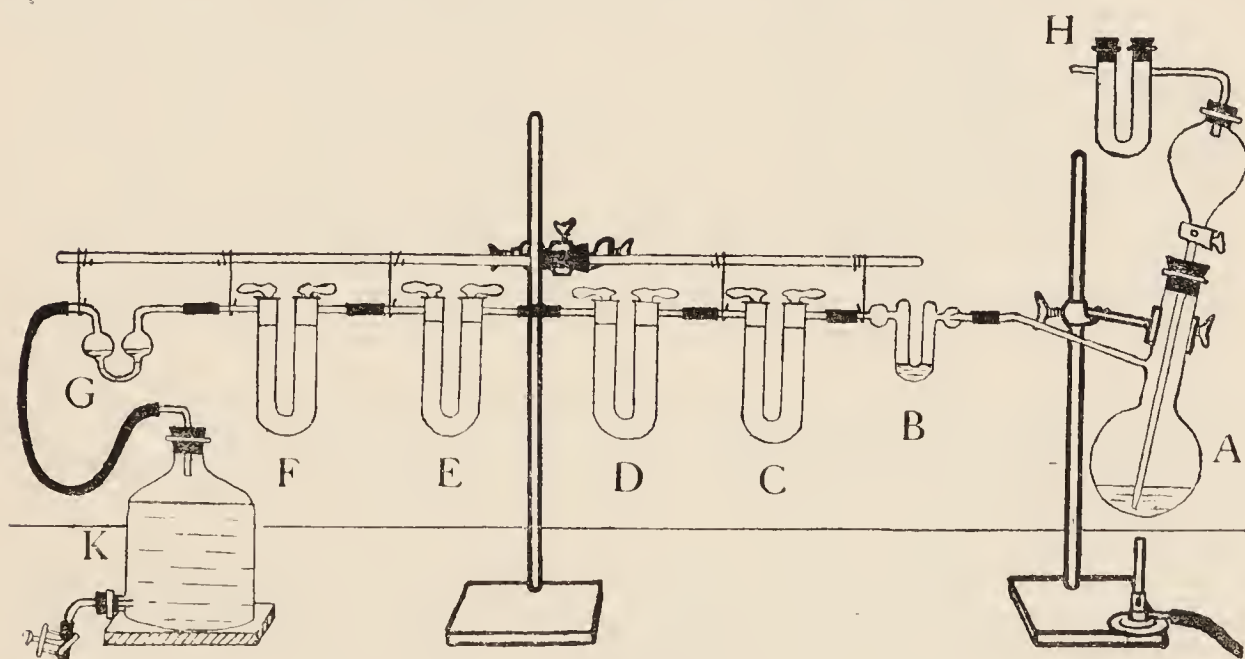


FIG. 59.

the latter should reach almost to the bottom of the flask, and the end should be drawn out to a point.

B. A U-tube, the open ends of which are sealed in the blowpipe flame, containing concentrated sulphuric acid. The acid is drawn in through one of the side-tubes, and the quantity is carefully adjusted until it is sufficient, *but no more than sufficient*, to seal the bend of the U-tube. The acid on the side-tube is volatilised by heating in a small flame,

C. A **U**-tube containing granulated pumice which has been soaked in concentrated copper sulphate solution, and afterwards heated for several hours in an air-oven at 160° in order partially to dehydrate the copper sulphate. The object of this tube is to retain hydrogen sulphide arising from decomposable sulphides present in the substance, and any hydrochloric acid that may be carried over with the carbon dioxide.

D. A **U**-tube containing moderately fine granular calcium chloride, free from powder. The calcium chloride is introduced through a cylinder of glazed paper, and the tube is filled to within 2 cm. of the side-tubes. Loose wads of glass wool are then placed in each limb, any calcium chloride

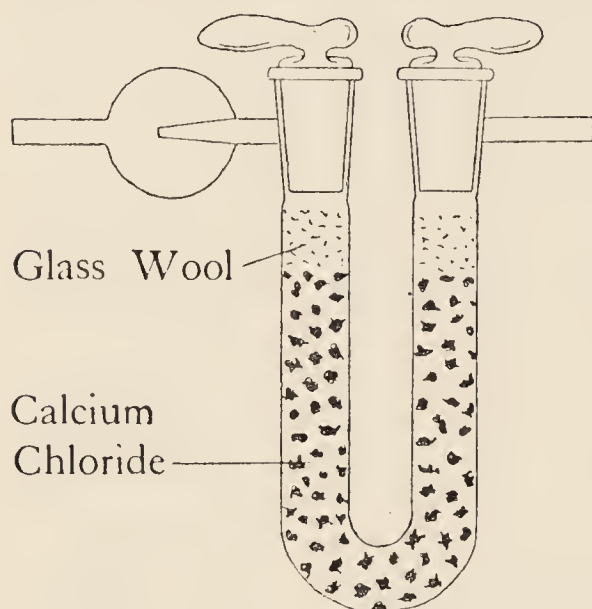


FIG. 60.

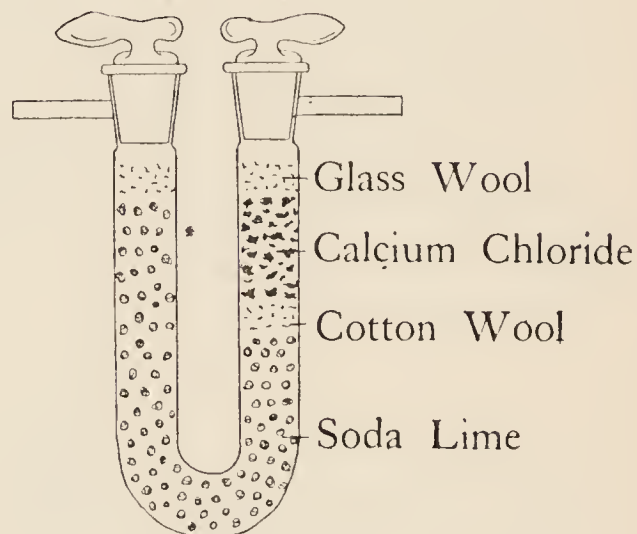


FIG. 61.

adhering to the upper part of the tube is removed, and the taps are made gas-tight with the minimum quantity of grease (Fig. 60).

In order to remove from the calcium chloride any free lime or basic chloride, which absorb carbon dioxide, a slow current of dry carbon dioxide (p. 148) is passed through the tube for five minutes in order to displace the air; the outlet tap of the **U**-tube is then closed, and the tube is left attached to the Kipp generator for several hours or overnight. The carbon dioxide in the tube is then displaced by passing dry air through it for about fifteen minutes.

E. and F. Two **U**-tubes containing soda-lime¹ and

¹ Soda-lime quickly deteriorates if exposed to the air, and soon becomes useless for the absorption of carbon dioxide. For this reason it is best to obtain it in *small*, well-corked bottles.

calcium chloride. A small wad of cotton wool is placed near the middle of one limb, and fine granular soda-lime is introduced through a paper cylinder so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb (Fig. 61). The absorption of carbon dioxide by soda-lime takes place with evolution of heat, and loss of the water which is formed at the same time is prevented by the calcium chloride.

G. A pulsimeter and guard-tube, containing a few drops of concentrated sulphuric acid. The latter protects the calcium chloride in the last U-tube from atmospheric moisture, and also shows the rate at which air leaves the apparatus.

H. A tube containing soda-lime which removes carbon dioxide from the air that is finally drawn through the apparatus.

K. An aspirator; an inverted wash-bottle with the jet removed and supported on a retort-stand ring may be used. The flow of water is regulated by means of a screw-clip.

The best form of U-tube is provided with hollow, ground-in glass taps. If plain U-tubes are used, they may be closed with tightly fitting rubber stoppers, or with ordinary well-softened corks which are cut off flush with the top of the tube, and made gas-tight by brushing over with melted paraffin wax.

The contents of the U-tubes must be protected from atmospheric moisture and carbon dioxide. This is accomplished with the first form of U-tube by simply turning the taps; plain U-tubes must be provided with caps, fitted over the side-tubes, and made from short pieces of rubber tubing closed with plugs of glass rod. The U-tubes are supported by wire hooks attached to a glass rod held in a clamp. They are connected with each other by means of short pieces of thick-walled rubber tubing (pressure tubing) which are lubricated by rubbing the inner surface with a little graphite, any excess of which is carefully removed.

Procedure.—Carefully wipe the two soda-lime absorption tubes and leave them in the balance-room for fifteen minutes before weighing. (Remove the rubber caps before weighing.)

In general, the amount of carbonate taken for analysis should be so chosen that the increase in weight of the soda-lime tube is about 0.3 gram.

Weigh the carbonate (*e.g.* about 1 gram of calcspar) in a small tube, about 1 in. long and $\frac{1}{2}$ in. wide. Place the tube and contents in the distilling flask, and moisten with a few drops of water.

Set up the apparatus, as shown in Fig. 59. The U-tubes are attached one after the other beginning with B, and the ends of the glass tubes should be brought close together inside each rubber junction. The absorption tubes E and F must be so placed that *the limbs containing calcium chloride are turned towards the aspirator*. The aspirator is not connected at this stage.

Test the apparatus in order to find if it is gas-tight, as follows:—Attach a piece of glass tubing to the guard-tube G, and dip the tube into a beaker of water. Open all the taps, apply gentle suction at H in order to lift a column of water in the tube attached to G, and then close the tap of the dropping funnel. The apparatus may be considered gas-tight if the level of the water in the tube remains constant for several minutes.

Now place about 20 c.c. of dilute hydrochloric acid in the dropping funnel, open the tap carefully, and regulate the flow of acid and the evolution of gas so that about two bubbles per second pass through the acid in B.

After a slight excess of acid has been added, and when the evolution of gas has become slow, close the tap of the dropping funnel and (by means of a pipette) remove any acid remaining in the latter. Warm the contents of the flask very gradually with a small flame until the liquid just boils. Boil gently for about one minute, then lower the flame until boiling just ceases, *and open the tap of the dropping funnel*. Attach the aspirator and the soda-lime tube H, and draw a slow current of air through the apparatus. As soon as the first soda-lime tube becomes cold, extinguish the flame, and continue the current of air for fifteen minutes more.

Detach the soda-lime tubes and, after wiping them, leave them in the balance-room for about half an hour before weighing. The weight of the tube F should remain practi-

cally constant, any increase amounting to not more than about 1 mgrm. A decided increase in weight shows either that the experiment was conducted too hurriedly, or that the soda-lime is unsatisfactory.

It is usual to calculate the percentage of carbonate in the substance as CO_2 .

Indirect Method.

OUTLINE OF METHOD.—A weighed quantity of the substance is decomposed by dilute acid in an apparatus of special design, and the loss in weight of the apparatus, due to the escape of carbon dioxide, is ascertained.

This method is not so accurate as the direct method (absorption by soda-lime), and its use is preferably restricted

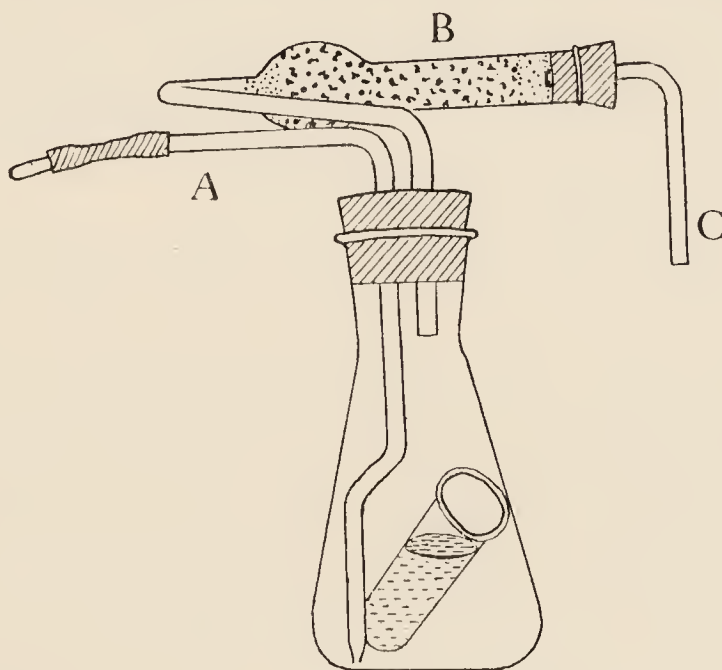


FIG. 62.

to the analysis of carbonates that can be decomposed by dilute *sulphuric* acid. If hydrochloric acid is used, its volatility makes it somewhat difficult to prevent loss of traces of that acid, and the result may be slightly high.

The Apparatus (Fig. 62) consists of a small, wide-mouthed flask (100 to 120 c.c.), of thin glass for the sake of lightness. The flask is fitted with a rubber stopper, through which pass a calcium chloride drying-tube and a tube that reaches nearly to the bottom of the flask and is drawn to a point at its lower end. The drying-tube is filled with granular calcium chloride with glass-wool plugs at either end, and the calcium chloride must be saturated with carbon dioxide, as

previously described (see the direct method). If the carbonate is to be decomposed by means of hydrochloric acid, one-third of the drying-tube B is filled with granular pumice which has been soaked in concentrated copper sulphate solution and dried at 160° , and two-thirds with calcium chloride. The acid required for the decomposition of the carbonate is contained in a small test-tube, the length of which is so adjusted that the tube will stand obliquely in the flask, but cannot fall into a horizontal position. The tubes A and C are provided with rubber caps closed with short pieces of glass rod. Two additional straight calcium chloride tubes are also required.

Procedure.—Weigh the substance in the dry flask (*e.g.* about 2 grams of sodium carbonate crystals). Measure a slight excess of dilute sulphuric acid (5 to 10 c.c.) into the small test-tube, and fit the apparatus together. Allow it to remain in the balance-room for fifteen minutes, remove the rubber caps, and weigh.

Replace the cap on tube A, attach one of the supplementary calcium chloride tubes to C (in order to protect the contents of B from atmospheric moisture) and, by carefully tilting the flask, allow the acid, a few drops at a time, to come into contact with the carbonate. The evolution of carbon dioxide must not be rapid, otherwise moisture may be carried away with the gas. When the whole of the acid has been mixed with the carbonate and effervescence has ceased, warm the flask cautiously with a *very small* flame until the liquid is heated almost to the boiling-point. Then attach an aspirator to C, and, the aspiration having been started, remove the cap on A, attach a calcium chloride tube to A, and draw a slow current of dry air through the apparatus for ten minutes. Remove the flame, continue the air current for ten minutes more, replace the caps on A and C, and, after an interval of about thirty minutes, weigh the apparatus (without the caps).

The loss in weight represents the carbon dioxide expelled from the carbonate.

Aspirator.—An evacuated Winchester quart bottle, closed with a rubber stopper through which passes a tube provided with a tap, makes a very convenient aspirator.

CHLORATE.

Chlorate is usually determined by reduction to chloride (p. 130) and determination of the chloride by one or other of the methods mentioned below.

Volumetric methods for the determination of chlorate are described on pp. 113 and 130.

CHLORIDE.

Chloride may be determined volumetrically by the methods given on pp. 125 and 129.

The gravimetric determination of chloride is described on p. 164.

For methods of separately determining chloride, bromide, and iodide in mixtures, reference may be made to R. M. Caven (*J. Soc. Chem. Ind.*, 1909, **28**, 505).

CHROMIUM.

The volumetric method described on p. 103 is convenient and accurate.

In order to separate chromium from other metals, it is first oxidised to chromate by fusion with sodium peroxide, or with a mixture of sodium carbonate and potassium nitrate; the chromate is determined volumetrically by the method already indicated, or gravimetrically as described on p. 222.

In the absence of all metals other than the alkalis, chromium may be determined by precipitation as hydroxide and conversion into oxide. The procedure is identical with that described under Aluminium on p. 163.

Chromic Hydroxide, when freshly precipitated, is a grey-green flocculent substance, insoluble in water. It is readily soluble in acids and in sodium hydroxide. It is sparingly soluble in ammonia, yielding a violet-red solution; on boiling this solution, the ammonia is expelled and the chromic hydroxide is precipitated. When dried at 100° , it loses water of hydration and becomes bluish-green. On ignition it is converted into chromic oxide, Cr_2O_3 .

Chromic Oxide is a dark green powder which may be ignited strongly without loss of weight. The oxide, after strong ignition, is insoluble in hydrochloric acid.

CHROMATE AND DICHROMATE.

Chromate and dichromate are usually determined volumetrically (p. 103). If the method is practicable, the gravimetric determination as mercurous chromate is easy and accurate. Chromate (or dichromate) may also be determined gravimetrically by reduction to a chromic salt, followed by precipitation as chromic hydroxide (see under Chromium).

Forms in which Chromate is precipitated.

Mercurous Chromate.—The presence of chloride or sulphate, except in small amount, renders this method inaccurate.

Barium Chromate.—Chloride does not interfere with the use of this method, but sulphate must, of course, be absent. The properties of barium chromate are described on p. 208.

Determination of Chromate as Mercurous Chromate.

OUTLINE OF METHOD.—The chromate is precipitated as mercurous chromate, which on ignition is decomposed, leaving chromic oxide, Cr_2O_3 .

Mercurous Chromate.—On addition of mercurous nitrate to a chromate, a brown precipitate of a basic salt separates. This quickly changes to the bright red, normal salt, Hg_2CrO_4 . Mercurous chromate is insoluble in water and in very dilute nitric acid. On ignition, it is converted into chromic oxide (for the properties of chromic oxide, see p. 221). If the mercurous chromate is contaminated with much mercurous chloride, the precipitate is bulky and inconvenient, and chromic oxide is lost during the ignition.

Procedure.—Heat the neutral or slightly acid solution, and add mercurous nitrate until precipitation is complete. Keep the solution hot until the precipitate becomes bright red. Then add ammonia cautiously until a small quantity of a dark grey precipitate permanently forms. Heat until boiling, then cool, filter, and wash with a dilute mercurous nitrate solution. Dry the precipitate and the filter. Burn

the filter before the addition of the precipitate. Ignite very gently at first and in a good draught, and finally ignite with the blowpipe. (**Caution.**—*The vapour given off during the ignition of the mercurous chromate is poisonous.*) Cool, and weigh the Cr_2O_3 .

COBALT.

Cobalt is determined after removal of metals precipitated by hydrogen sulphide in acid solution. From the analytical point of view, cobalt shows an extremely close relationship to nickel and, with one exception, the methods indicated on p. 238 for the determination of nickel may be used without modification for cobalt. Cobalt (unlike nickel) is not precipitated by diacetyldioxime, and one of the best methods of separating cobalt from nickel is based on this fact (see p. 241); another method of separation is described below.

Forms in which Cobalt is precipitated.

Cobalt Sulphide.—Precipitation with ammonium sulphide serves to separate cobalt, nickel, manganese, etc., from the alkalis and alkaline earths. Cobalt (and nickel) may be separated from manganese by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Cobaltic Hydroxide.—Cobaltic hydroxide is precipitated by bromine and sodium hydroxide, and the hydroxide is reduced to metallic cobalt, as described under Nickel (p. 239).

Cobalt Ammonium Phosphate.—The procedure is identical with that described for zinc on p. 263. The precipitate may be weighed as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ after drying at 105° , or it may be converted into cobalt pyrophosphate by gentle ignition.

Cobalt Salt of Nitroso- β -naphthol.—This cobalt salt is insoluble in hydrochloric acid, whereas the corresponding nickel salt is soluble, and the method is very useful for the separation of a small quantity of cobalt from a comparatively large quantity of nickel.

Metallic Cobalt (Electrolytic).—The procedure is identical with that described for nickel on p. 185.

Determination of Cobalt by the Nitroso- β -naphthol Method.

OUTLINE OF METHOD.—The cobalt is precipitated by means of nitroso- β -naphthol dissolved in acetic acid. The precipitate is washed, dried, and ignited. The cobalt oxide is ignited in an atmosphere of hydrogen and the metallic cobalt weighed.

Nitroso- β -naphthol, $C_{10}H_6 \cdot O \cdot NOH$ or $C_{10}H_6 \cdot OH \cdot NO$, is a yellow, crystalline substance, insoluble in water. The reagent is a freshly prepared solution obtained by dissolving 1 gram of the solid in 40 c.c. of glacial acetic acid, adding an equal volume of water, and filtering. The cobaltic compound, $(C_{10}H_6 \cdot O \cdot NO)_3Co$, is obtained as a voluminous, brick-red precipitate which is insoluble in dilute hydrochloric acid. The nickelous compound, $(C_{10}H_6 \cdot O \cdot NO)_2Ni$, is soluble in hydrochloric acid.

Procedure.—Dilute the solution, containing not more than 0.05 gram of cobalt as sulphate or chloride, to 150 c.c. and add 5 c.c. of concentrated hydrochloric acid. Heat to about 70° and add 25 to 50 c.c. (according to the amount of cobalt) of the hot reagent. Allow the precipitate to settle, and ascertain whether precipitation is complete by adding more reagent to the clear solution. Set aside for at least six hours. Filter through an 11-cm. paper. Wash the precipitate first with cold water, then with hot, dilute (1:2) hydrochloric acid (in order to remove the nickel salt), and finally with hot water until free from acid. Dry the precipitate. Incinerate the paper together with the precipitate and about a decigram of pure oxalic acid (in order to facilitate removal of carbon) in a Rose crucible; raise the temperature very cautiously, and ignite finally with a Méker burner. Reduce the cobalt oxide (mainly Co_3O_4) by heating in a current of hydrogen. Cool, and weigh the metallic cobalt.

COPPER.

Copper may be determined volumetrically (see p. 109). In gravimetric analysis, copper is precipitated in acid solution, together with many other metals, by hydrogen sulphide.

A colorimetric method for the determination of traces of copper is described on p. 195.

Forms in which Copper is precipitated.

Cupric Sulphide.—Precipitation is complete even in strongly acid solution, and this method is therefore used to separate copper from iron, zinc, etc. It does not separate copper from bismuth, mercury, etc. See pp. 174 and 268.

Cupric Oxide.—This is a convenient and accurate method, but is seldom applicable, as no other metals that give insoluble oxides may be present. For details, see p. 166.

Cuprous Thiocyanate.—Since most thiocyanates are soluble, this method is sometimes useful for the separation of copper from other metals.

Metallic Copper (Electrolytic method).—This is probably the best method for separating copper from the other metals precipitated with it by hydrogen sulphide in acid solution. For details, see pp. 181 and 183.

Determination of Copper as Cuprous Thiocyanate.

OUTLINE OF METHOD.—The copper is precipitated with ammonium thiocyanate in presence of sulphurous acid, and is weighed as cuprous thiocyanate after drying at 140° to 150° .

Cuprous Thiocyanate, CuCNS , is a pure white, crystalline precipitate, almost insoluble in water and in dilute hydrochloric, sulphuric, and sulphurous acids. It may be dried without decomposition at temperatures not exceeding 150° .

Procedure.—The solution should be made *slightly* acid with sulphuric acid. (Nitrates or other oxidising agents, if present, must be removed by evaporation with sulphuric acid.) Add excess of sulphurous acid, warm, and to the warm solution add ammonium thiocyanate, drop by drop, with constant stirring. The greenish precipitate becomes pure white when stirred for some time. When the precipitate has settled (which may be after some hours), filter through a Gooch crucible, and wash with cold water until ferric chloride gives no coloration with the washings. Wash finally several times with 20 per cent. alcohol, dry at a temperature not exceeding 150° , and weigh as CuCNS .

FLUORIDE.

Both gravimetric and volumetric methods are used for the determination of fluoride. Gravimetrically, fluoride is usually precipitated and weighed as calcium fluoride. One of the simplest methods of determining fluorine in fluorides, or in silicates decomposable by sulphuric acid, is to expel the fluorine as silicon fluoride and measure the volume of the gas. A full description of various methods of determination is given in Mellor's *Quantitative Inorganic Analysis*.

Determination of Fluoride in a Silicate Rock.

OUTLINE OF METHOD.—The powdered substance is fused with sodium carbonate and the resulting mass extracted with water and filtered. After removal of the silica and bases from the solution by means of ammonium carbonate, calcium chloride is added, and the precipitated calcium fluoride and calcium carbonate is ignited. The calcium carbonate is removed with acetic acid, and the residual calcium fluoride is ignited and weighed.

Calcium Fluoride is a white, gelatinous precipitate, sparingly soluble in hydrochloric and nitric acids, and nearly insoluble in acetic acid. It is more soluble in presence of ammonium salts. The precipitate is very difficult to filter, but if precipitated together with some calcium carbonate the filtration is much easier. Calcium fluoride cannot be completely decomposed by fusion with sodium carbonate unless it is mixed with silica or a silicate.

Procedure.—Weigh accurately in a platinum crucible about 2 grams of the rock powder and mix it with 12 grams of dry sodium carbonate. (In the case of a fluoride containing but little silica, 4 grams of silicic acid must also be added.) Heat the mixture gradually to redness, and maintain the temperature until effervescence ceases (*cf.* p. 253). Do not use the blowpipe. After cooling, place the crucible in a large porcelain basin or casserole, and extract the mass thoroughly with hot water, taking care to break down any large lumps. Filter, and wash with hot water. The filtrate contains all the fluoride.

Add about 10 grams of ammonium carbonate and set aside for about twelve hours in a warm place. Filter the pre-

precipitated silica and alumina, and wash with dilute ammonium carbonate solution. Heat the covered beaker containing the filtrate on the steam-bath until the ammonium carbonate is decomposed and the evolution of carbon dioxide ceases. In order to remove the last traces of silica, add about 5 c.c. of a solution of precipitated zinc oxide in 10 per cent. ammonia, and evaporate until the smell of ammonia disappears. Filter, and wash with water.

Add dilute nitric acid to the filtrate until the alkali carbonate is nearly, but not entirely, decomposed. If too much acid is added, make the solution alkaline again with sodium carbonate. Then add excess of calcium chloride, and heat until boiling. Filter the precipitated calcium fluoride and calcium carbonate, wash with hot water, dry, and ignite at a low red heat in a platinum crucible. After cooling, add sufficient acetic acid to dissolve the calcium carbonate and oxide; warm the covered crucible on the steam-bath until effervescence ceases, and then evaporate to dryness. Extract with hot water containing a few drops of acetic acid, filter, wash, and ignite the residue. Repeat the extraction with very dilute acetic acid, and finally ignite to faint redness and weigh the CaF_2 .

It is advisable to check the result by converting the calcium fluoride into calcium sulphate. Add a few drops of concentrated sulphuric acid and evaporate carefully (Fig. 13 or 14, p. 24). Ignite at a low red heat, and weigh the CaSO_4 .

HYPOCHLORITE.

The only common hypochlorites are those of calcium and sodium. Volumetric methods are described on pp. 115 and 133, and a gas-volumetric method on p. 327.

IODIDE.

Iodide is readily determined by the volumetric methods described on pp. 125 and 129.

It may also be determined gravimetrically by precipitation as silver iodide. The procedure is identical with that given for the determination of chloride (p. 164), except that there is no need to protect the precipitate from light.

Silver Iodide is much less soluble in almost all solvents than either the chloride or bromide. The solubility in water is negligibly small (0.003 mgrm. per litre at 20°). It is practically insoluble in dilute nitric acid and very sparingly soluble in ammonia (35 mgrms. per litre in 10 per cent. ammonia at 15°). It is appreciably soluble in concentrated silver nitrate and other salt solutions. Silver iodide fuses, without decomposition, at 552°.

IRON.

On account of its rapidity and accuracy, the volumetric determination of iron (pp. 94 and 134) is preferable to any gravimetric method.

The volumetric method may often be applied after the iron has been separated gravimetrically from most other metals, and it is one of the best methods for the determination of the iron in a mixed precipitate of ferric and aluminium oxides (compare pp. 283 and 287).

In gravimetric analysis, iron is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. It is sometimes precipitated, together with aluminium, chromium, titanium, manganese, nickel, cobalt, and zinc, by ammonium sulphide, and is then separated from the other metals. In absence of the other metals of this group, it is preferable to precipitate iron and aluminium as hydroxides with ammonia.

The separation of iron from manganese, etc., is a matter of some difficulty. The "cupferron" method, described on the next page, is easier, more rapid, and no less accurate than the older basic acetate method.

A colorimetric method for the determination of traces of iron is described on p. 192.

Forms in which Iron is precipitated.

If not already in the ferric state, the iron is always oxidised before precipitation.

Ferric Hydroxide.—This is the easiest gravimetric method for the determination of iron, but is of limited applicability. For details, see p. 159.

Basic Ferric Acetate.—This method provides a separation from manganese, chromium, zinc, nickel, and cobalt, but aluminium is precipitated with the iron. For details, see under Aluminium, p. 203.

Ferric Salt of Nitrosophenyl Hydroxylamine (“Cupferron” Method).—Iron is precipitated by “cupferron” from strongly acid solutions. This method provides a complete separation of iron from all metals other than the silver and copper groups, and is particularly useful for the separation of iron from aluminium, manganese, and chromium.

Determination of Iron by the “Cupferron” Method.

OUTLINE OF METHOD.—The iron (in the ferric state) is precipitated from a strongly acid solution by “cupferron,” and the precipitate is converted into ferric oxide by ignition.

Cupferron is the ammonium salt of nitrosophenyl hydroxylamine, $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$. (For the method of preparation of cupferron, see Appendix.) It precipitates most of the heavy metals from neutral solutions as insoluble salts. From strongly acid solutions, however, only the cupric and ferric compounds are precipitated. Copper is readily removed from the solution, and the method is therefore useful for the separation of iron from manganese, aluminium, etc. The separation is remarkably complete, but in cases where large amounts of aluminium, manganese, or chromium are present, a second precipitation is advisable.

The precipitate of the ferric salt is rather bulky, and the amount of material taken should therefore be such as to yield about 0.1 gram of ferric oxide. The solubility of the precipitate appears to be negligible, even in 4N hydrochloric acid.

Procedure.—To the solution add 20 c.c. of concentrated hydrochloric acid and dilute to 100 c.c. Dissolve about 3 grams of cupferron in 50 c.c. of cold water, and add it slowly and with constant stirring to the ferric salt solution. A brownish-red precipitate, which is partly crystalline and partly amorphous, separates. Stir well, but do not heat the solution.

Filter with suction. If the precipitate adheres tenaciously to the beaker, dissolve it in a little ether and then remove the ether by addition of a little boiling water.

Wash with cold water until almost free from acid, then twice with dilute (6N) ammonia, and finally twice with water. Place the wet paper and precipitate in a porcelain crucible and heat gently until no more inflammable gases are given off. Ignite, and weigh the ferric oxide obtained.

LEAD.

In the analysis of a mixture, lead is usually determined as sulphate, although the chromate method is preferable if it can be used. The separation of lead from calcium by precipitation as sulphide is described in connection with the analysis of glass (p. 292).

A colorimetric method for the determination of traces of lead is described on p. 198.

Forms in which Lead is precipitated.

Lead Sulphate.—This method provides a separation from all metals except barium, strontium, calcium, and mercury.

Lead Chromate.—This method is more accurate than the sulphate method, but is limited in applicability on account of the general insolubility of chromates.

Lead Peroxide (Electrolytic).—Lead may be separated from almost all other metals by this method. For details, see p. 187.

Determination of Lead as Sulphate.

OUTLINE OF METHOD.—The solution is evaporated with concentrated sulphuric acid until all hydrochloric or nitric acid is expelled. After dilution, the lead sulphate is filtered, washed with alcohol, dried, and weighed as PbSO_4 .

Lead Sulphate is a heavy, white powder which is sparingly soluble in water. One litre of water at 18° dissolves about 40 mgrms. of the salt (82 mgrms. according to one authority). It is much less soluble in dilute sulphuric acid, but with increasing concentration of sulphuric acid the solubility again increases. It is readily soluble in hot concentrated hydrochloric and nitric acids. It is soluble in solutions of almost all ammonium salts and in solutions of alkali hydroxides, but is almost insoluble in alcohol. It may be heated to a bright

red heat without decomposition if reducing gases are excluded from the crucible. At a red heat, it is readily reduced by carbonaceous matter, with loss of lead by volatilisation.

Procedure.—To the lead solution add 3 c.c. of concentrated sulphuric acid, and evaporate in a porcelain basin on the steam-bath and then over a rose burner until dense white fumes are evolved. Cool, dilute to about 100 c.c. with cold water, and stir. The precipitate may be filtered more readily if it is kept for a few hours before filtration.

Filter through a Gooch crucible, wash two or three times with sulphuric acid (approximately normal), and then wash with alcohol until free from acid.

If the original solution contained other metals, the precipitate must be washed from six to eight times with the minimum quantity of normal sulphuric acid before using alcohol; the alcohol washings are rejected.

Dry at 100° , place the Gooch crucible inside a nickel crucible, and heat strongly until of constant weight.

Determination of Lead as Chromate.

OUTLINE OF METHOD.—The lead is precipitated as chromate by the addition of potassium chromate (or dichromate). The precipitate is collected in a Gooch crucible, dried at 120° , and weighed as PbCrO_4 .

Lead Chromate is almost insoluble in water and in acetic acid (1 litre of water dissolves 0.1 mgrm. at 18°), slightly soluble in nitric acid, and readily soluble in alkali solutions. It may be dried completely at 100° , but loses oxygen if heated to its melting point.

Procedure.—If the solution is neutral or alkaline, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate (5 to 10 grams) to replace the nitric acid by acetic acid. To the hot solution add potassium chromate (2 per cent. solution) in slight excess (10 c.c. may be sufficient). Place the beaker on the steam-bath until the precipitate settles. Examine the supernatant liquid, which must be coloured slightly yellow. Filter through a Gooch crucible, wash thoroughly with hot water, and dry at 120° .

MAGNESIUM.

On account of their alkaline character, magnesium carbonate and hydroxide may be determined volumetrically, but there is no volumetric process applicable to magnesium salts in general.

In the analysis of a mixture, magnesium is always determined after removal of the copper, iron, zinc, and calcium groups. A typical example of the separation of magnesium from calcium and other metals is described on p. 281.

The only gravimetric method for the determination of magnesium has already been described (p. 172).

MANGANESE.

Manganese may be determined volumetrically (p. 87).

In gravimetric analysis, manganese is always determined after removal of the metals precipitated in acid solution by hydrogen sulphide. Hillebrand, in his *Analysis of Silicate and Carbonate Rocks*, states that "the gravimetric determination of manganese in small amount seems to be more of a stumbling block to the average chemist than that of almost any other of the frequently occurring elements in mineral analysis. This is due almost always to incomplete prior precipitation of elements which later suffer co-precipitation with the manganese."

A colorimetric method for the determination of traces of manganese is described on p. 199.

Forms in which Manganese is precipitated.

Manganous Carbonate.—This method is applicable in the absence of other metals that form insoluble carbonates, and only the alkalis and ammonium salts may be present.

Manganese Dioxide (Hydrated).—Precipitation in this form by means of ammonium persulphate provides a method of separation from chromium. If more than traces of zinc nickel, or cobalt are present, a second precipitation is necessary for complete separation.

Manganous Sulphide.—In this form, manganese is precipitated by means of ammonium sulphide along with nickel

and cobalt. The nickel and cobalt are removed by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Manganese Ammonium Phosphate.—On account of the general insolubility of phosphates, this method is of limited applicability, but the precipitate obtained is so easily filtered that the method has marked advantages when no separation from other metals is required. The procedure is identical with that described for zinc in presence of alkalis (p. 264). Ammonium chloride is added prior to the precipitation, and the precipitate is converted into the pyrophosphate, $\text{Mn}_2\text{P}_2\text{O}_7$, by gentle ignition.

Determination of Manganese as Carbonate.

OUTLINE OF METHOD.—The manganese is precipitated as manganous carbonate by means of ammonium carbonate. By ignition, first in air and then in a current of carbon dioxide, the precipitate is converted into Mn_3O_4 , which is weighed; or it may be converted into and weighed in one or other of the forms mentioned below.

Manganous Carbonate is a buff-coloured powder which darkens somewhat on exposure to air and is sometimes difficult to filter. It is practically insoluble in water and in solutions of ammonium salts. It dissolves in acids and is slightly soluble in solutions of alkali carbonates.

At a high temperature, with access of air, manganous carbonate is converted mainly into Mn_3O_4 , together with traces of Mn_2O_3 and MnO_2 , the actual composition of the residue depending on the manner of ignition. This mixture of oxides may be converted quantitatively into—

- (1) MnO (green), by heating to a high temperature in a current of hydrogen;
- (2) Mn_3O_4 (brown), by heating to a high temperature in a current of carbon dioxide;
- (3) Mn_2O_3 (black), by heating to low redness in a current of oxygen;
- (4) MnS (green), by heating with sulphur in hydrogen;
- (5) MnSO_4 (white), by adding sulphuric acid and heating to low redness.

Procedure.—If the manganese is present as permanganate it must first be reduced to a manganous salt by means of sulphur dioxide and the excess of sulphur dioxide expelled by boiling.

Neutralise the solution with ammonia, add 10 grams of ammonium chloride and a slight excess of ammonium carbonate. Allow the beaker to remain on a gently heated steam-bath until the precipitate has settled completely. Filter, and wash the precipitate with hot water. Incinerate the filter together with the precipitate in a Rose crucible, and ignite the precipitate in the open crucible for ten minutes with a Méker or Teclu burner. Then pass a slow current of carbon dioxide into the crucible, and heat again to a high temperature for ten minutes. Cool in an atmosphere of carbon dioxide, and weigh as Mn_3O_4 . Repeat until constant weight is attained.

In order to check the result, heat the oxide with a Méker burner in a *rapid* current of hydrogen for five minutes, and weigh as MnO . Repeat until the weight is constant.

Determination of Manganese as Dioxide.

OUTLINE OF METHOD.—The manganese is precipitated as hydrated manganese dioxide by boiling an acidified solution with ammonium persulphate. The dioxide is converted by ignition into a lower oxide, which is weighed.

Hydrated Manganese Dioxide is a brownish-black precipitate which is insoluble in water, alkalis, dilute sulphuric or nitric acid. It is somewhat soluble in concentrated nitric acid, readily soluble in hydrochloric acid with evolution of chlorine, and in concentrated sulphuric acid with evolution of oxygen. It is insoluble in solutions of ammonium salts. If precipitated in alkaline solution, it occludes alkali which cannot be removed by washing. The dioxide itself is unsuitable for weighing and is always converted into one of the lower oxides by ignition, as already described.

Procedure.—Dilute the solution, which should be slightly acid with sulphuric acid, but must contain no other acid, to 200 c.c. To the cold solution, add 2 grams of ammonium persulphate dissolved in about 50 c.c. of water, and heat quickly until boiling. Add ammonia until the solution is

faintly alkaline. Boil for two minutes, filter at once without cooling, and wash the precipitate thoroughly with hot water. The filtrate should be colourless; set it aside on the steam-bath for an hour. No further precipitate should form, but if there is any, filter, and add it to the main precipitate.

Incinerate the filter together with the precipitate in a Rose crucible, and convert into a lower oxide suitable for weighing, as already described.

The above method affords a complete separation from chromium. If other metals, such as iron, zinc, nickel, and cobalt are present, a second precipitation is necessary, and even then the separation may not be complete. Dissolve the precipitate, after thorough washing, in hot concentrated hydrochloric acid containing a little sulphurous acid. Add 1 c.c. of concentrated sulphuric acid, evaporate until the hydrochloric acid is expelled, cool, and dilute with water. Reprecipitate as before.

Notes.—(1) The conditions for the precipitation must be closely adhered to, otherwise precipitation is incomplete.

(2) The purity of the ammonium persulphate should be tested. There should be no precipitation of alumina when a solution is boiled with ammonia. No weighable residue should be left after ignition of 2 grams in a platinum crucible.

MERCURY.

The volumetric method described on p. 130 is convenient and accurate.

Forms in which Mercury is precipitated.

Mercuric Sulphide.—The mercury must all be present as a mercuric salt. This method is recommended when applicable, *i.e.* in absence of those metals that are precipitated in a similar manner.

Metallic Mercury.—This method is useful for separating mercury from all other metals. It is applicable to mercury in any form of combination.

Determination of Mercury as Sulphide.

OUTLINE OF METHOD.—The mercury is precipitated with hydrogen sulphide in acid solution, and, after removal of any free sulphur by extraction with carbon disulphide, is weighed as HgS .

Mercuric Sulphide is inappreciably soluble in boiling dilute acids. It is slowly converted into mercury thionitrate and finally into soluble mercuric nitrate by boiling concentrated nitric acid. It may be dried completely at 100° ; at higher temperatures it volatilises unchanged.

Procedure.—The mercury, if not already in the mercuric state, must be oxidised by boiling with concentrated nitric acid. The presence of nitric acid in the solution is objectionable, because it gives sulphur with hydrogen sulphide, but it is not permissible to remove it by evaporation with hydrochloric acid since mercuric chloride would be volatilised in the process.

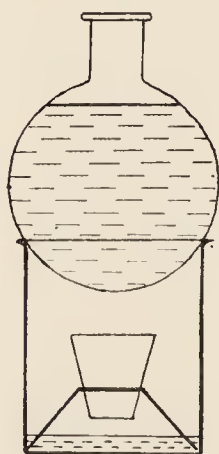


FIG. 63.

Saturate the cold solution with hydrogen sulphide, filter through a Gooch crucible, wash with cold water and then two or three times with alcohol. The sulphur in the precipitate is removed by extraction with carbon disulphide. Carbon disulphide usually contains some dissolved sulphur, and the following method of extraction is therefore recommended:—

Place the crucible on a glass triangle within a beaker which contains some carbon disulphide. Cover the beaker with a flask containing cold water (see Fig. 63), and heat the beaker on the steam-bath. Within an hour all the sulphur will be extracted. Wash twice with alcohol to remove carbon disulphide, and dry at 100° to 110° . Weigh the HgS .

Determination of Mercury as Metal.

OUTLINE OF METHOD.—The dry substance is heated with a mixture of quicklime, iron filings, and lead chromate. The mercury that is driven off is collected and weighed.

Procedure.—A convenient apparatus is that devised by Penfield for the determination of water in minerals. Close a piece of glass tubing (about 20 cm. in length and 5 mm. in diameter) at one end, and blow bulbs at A and B, Fig. 64.

Clean, dry, and weigh the tube. By means of the long funnel C, introduce 0.5 to 1.0 gram of the powdered material into the bulb A. Weigh the tube and contents.

Add some iron filings by means of the funnel C, from which any adhering trace of the substance has meanwhile been removed. Mix the substance and filings thoroughly by rotating the tube. Then add a mixture of one part quicklime,

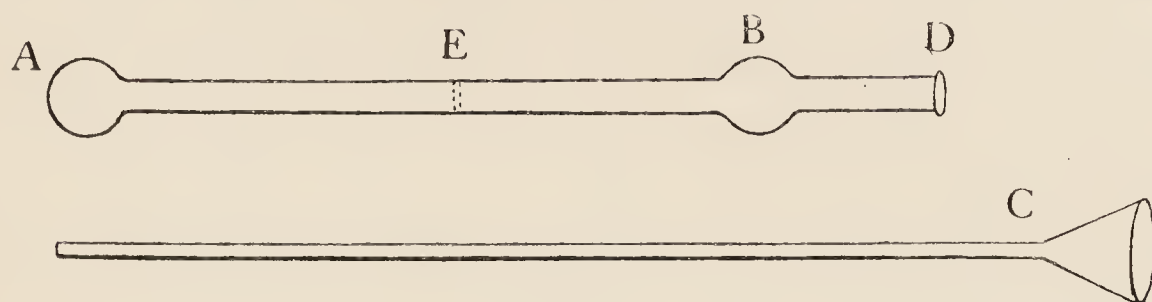


FIG. 64.

one part powdered (fused) lead chromate, and two parts iron filings, until about 8 cm. of the tube has been filled. Insert a small plug of asbestos, E, so that, after tapping the tube, only a very shallow air-channel remains over the mixture. Draw out the open end D into a fine capillary, as shown at F, Fig. 65.

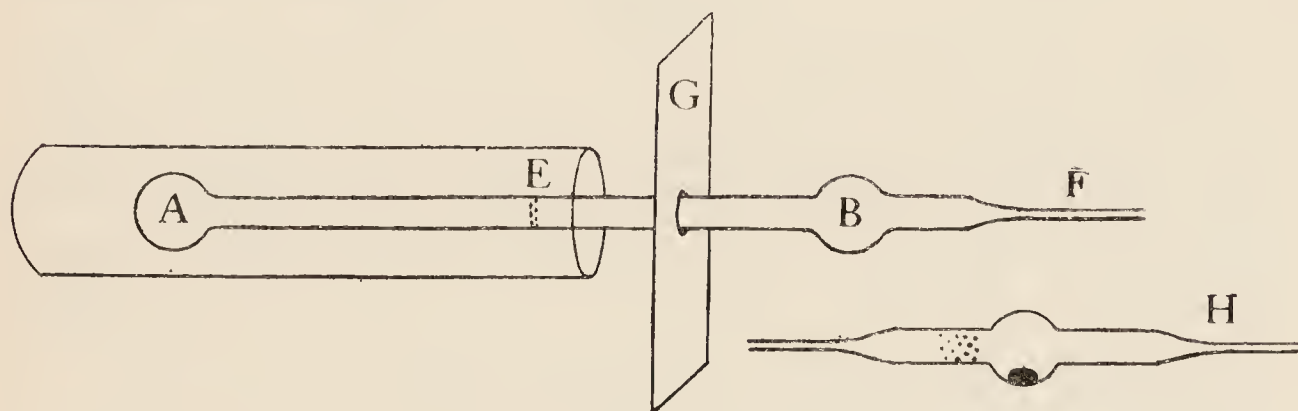


FIG. 65.

Place the prepared tube in an iron tube that can be heated by a flat-flame burner. (A piece of iron gas-pipe about 15 cm. by 1.5 cm., closed at the ends with plugs of asbestos, may be used.) Wrap the bulb A in some asbestos paper to prevent it coming into direct contact with the iron tube; if this precaution is omitted, the bulb becomes hot before the narrow portion of the tube, and the mercuric salt is partly volatilised without decomposition. Place an asbestos shield at G, and cover the bulb B with wet filter paper.

Heat the iron tube, at first with a small flame and at the end nearer G only. Gradually increase the flame and move it until the whole iron tube is heated to a low red heat. The apparatus must be almost horizontal, but with the end F slightly lower than the closed end, so that, on gently tapping the tube, any mercury that has condensed forms a globule and runs into the bulb B.

When all the mercury has distilled (usually within one hour), draw out the glass tube until the plug E is exposed. At the same time move the burner forward, so that the flame plays directly on the glass tube. As soon as the glass tube becomes red hot, draw it off about midway between the plug E and the bulb B. The mercury is thus obtained in a tube, as shown at H in Fig. 65.

To remove water, draw a current of dry air through the tube until the weight is constant. Shake out the main portion of the mercury, and remove the remainder by blowing air through the gently heated tube. (**Caution.**—*Mercury vapour is poisonous.*) Weigh the empty tube after cooling.

NICKEL.

Nickel is determined after removal of metals that are precipitated by hydrogen sulphide in acid solution. Although a pure nickel solution yields no precipitate with hydrogen sulphide in acid solution, some nickel is co-precipitated with the sulphides of the copper and arsenic group unless the solution is strongly acid.

A colorimetric method for the determination of traces of nickel is described on p. 201.

Forms in which Nickel is precipitated.

Nickel Sulphide.—Ammonium monosulphide precipitates nickel, together with the other metals of the iron and zinc group, and this method serves to separate nickel, iron, zinc, etc., from the alkalis and alkaline earths. Nickel sulphide is not precipitated from acid solutions, but the precipitated sulphide dissolves very slowly in cold dilute acids.

Nickel Peroxide.—This is a form in which nickel may be precipitated if no other metals are present.

Nickel Salt of Diacetyldioxime.—Nickel is precipitated in this form from alkaline or acetic acid solutions by means of an alcoholic solution of diacetyldioxime. This method separates nickel from cobalt, zinc, manganese, and (with appropriate modification) from iron, aluminium, chromium, and copper.

Metallic Nickel (Electrolytic).—This is a useful and accurate method for the determination of nickel. The method can be adapted to provide a separation of nickel from copper and other metals (see p. 185).

Determination of Nickel as Oxide.

OUTLINE OF METHOD.—The nickel is precipitated as nickel peroxide by means of bromine and sodium hydroxide. The precipitate is washed, dried, and ignited. It is then ignited in an atmosphere of hydrogen and the metallic nickel weighed.

Nickel Peroxide, Ni_2O_3 , when freshly precipitated, is a brownish-black substance which becomes darker on keeping. It is insoluble in hot or cold water and in alkaline solutions. The peroxide, unlike nickelous hydroxide, does not occlude alkali salts. On ignition, it is converted almost entirely into nickel oxide, NiO , but the composition of the residue varies considerably with the manner of ignition. Nickel oxide is completely reduced to metal by ignition in hydrogen. The metallic nickel may be contaminated with silica dissolved from the glass or porcelain vessel by the sodium hydroxide.

Procedure.—Dilute the nickel solution, which must not contain ammonium salts, in a porcelain beaker or basin to about 100 c.c., and add about 1 c.c. of bromine. Warm the solution, and precipitate the nickel with pure sodium hydroxide solution, avoiding excess. Heat until boiling. Any signs of greenish, nickelous hydroxide indicate that insufficient bromine has been added.

Filter, wash the precipitate with hot water (as far as possible by decantation), and dry. Incinerate the filter paper apart from the precipitate in a Rose crucible, add the precipitate, and ignite strongly for a few minutes. Allow the crucible to cool; pass a current of pure, dry hydrogen and heat the crucible to dull redness for about twenty

minutes. Continue the current of hydrogen until the crucible is cold, in order to prevent reoxidation. Repeat the ignition in hydrogen until the weight has become constant. The metallic nickel obtained in this way contains traces of silica. If the precipitation has been performed in a porcelain vessel without using a large excess of alkali, the amount of silica will be very small; but in all cases the silica should be determined and a correction applied. Dissolve the nickel in nitric acid, and evaporate to dryness. Moisten the residue with a few drops of concentrated acid, dilute with water, filter through a small filter paper, and wash until the residue is colourless. Incinerate the paper with the residue of silica, ignite, and weigh. Subtract the weight of silica from that of the impure nickel.

Determination of Nickel by the Diacetyldioxime Method.

OUTLINE OF METHOD.—The nickel is precipitated by adding diacetyldioxime dissolved in alcohol to a hot, slightly acid solution, and then adding ammonia or sodium acetate. The precipitate is collected in a Gooch crucible, dried at 120° , and weighed as $(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni}$.

Diacetyldioxime (Dimethylglyoxime),



is a white, crystalline substance, insoluble in water. The reagent is a 1 per cent. solution in absolute alcohol. It precipitates nickel as a voluminous, scarlet, crystalline salt, $(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni}$, easily soluble in mineral acids, and practically insoluble in water, acetic acid, and dilute ammonia.

Procedure.—Dilute the solution (which should contain not more than 0.05 to 0.06 gram of nickel, and should be slightly acid) to 200 c.c. and heat to about 80° . Add a large excess of the reagent (20 to 30 c.c.), and then add ammonia until the solution is very slightly alkaline (or add 2 to 3 grams of sodium acetate). Keep the solution hot for a few minutes, filter through a Gooch crucible, and wash the precipitate with hot water. Dry at 120° for an hour, and weigh. The precipitate contains 20.32 per cent. of nickel.

If cobalt is present, dilute the solution before precipitation so that 200 c.c. contains not more than 0.1 gram of cobalt, and add at least 50 c.c. of the reagent for 0.05 gram of nickel.

If copper is present, add sufficient ammonia to form the blue, soluble cuprammonium salt before precipitating the nickel. Filter and wash the precipitate. Dissolve it in hot nitric acid (1 : 3), and reprecipitate the nickel in presence of ammonia as before. (Full details are given on p. 271.)

If zinc is present, add sufficient ammonium chloride to prevent precipitation of the zinc by ammonia.

If iron, aluminium, or chromium is present, add sufficient tartaric acid (1 to 3 grams) to prevent their precipitation as hydroxides, dilute to 300 c.c., and add a large excess of the reagent.

If manganese is present, add sodium acetate (not ammonia) to complete the precipitation.

NITRATE.

Volumetric methods for the determination of nitrate are described on pp. 74 and 84, and a gas-volumetric method on p. 323.

The determination of traces of nitrate in natural waters is described on p. 348.

NITRITE.

A volumetric method for the determination of nitrite is described on p. 83, and gas-volumetric methods on pp. 323 and 325.

The determination of traces of nitrite in natural waters is described on p. 347.

PHOSPHATE.

Forms in which Phosphate is precipitated.

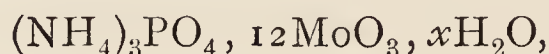
Ammonium Phospho-molybdate.—The chief value of this method is that it is applicable in presence of the alkaline earths, aluminium, and iron.

Magnesium Ammonium Phosphate.—This method is not applicable in presence of metallic radicals other than the alkalis.

Determination of Phosphate by the Molybdate Method.

OUTLINE OF METHOD.—The phosphate is precipitated in presence of nitric acid by ammonium molybdate. The precipitate is collected in a Gooch crucible, ignited, and weighed as phospho-molybdic anhydride, $24\text{MoO}_3, \text{P}_2\text{O}_5$.

Ammonium Phospho-molybdate,



is a bright yellow, crystalline substance, insoluble in dilute nitric and sulphuric acids, but somewhat soluble in hydrochloric acid. It is readily soluble in ammonia, and soluble also to some extent in solutions containing chlorides or ammonium salts (except the nitrate).

It may be weighed as the anhydrous salt after drying at 180° , but it is better to convert it into phospho-molybdic anhydride, $24\text{MoO}_3, \text{P}_2\text{O}_5$, by gentle ignition. The anhydride must not be heated too strongly, otherwise phosphoric anhydride will be volatilised and lost. Ammonium phospho-molybdate may also be determined indirectly by an alkali-metric method (p. 75).

On account of the small proportion of phosphorus in the final precipitate, an amount of substance containing about 10 mgrms. of P_2O_5 is ample for an analysis.

The following solutions are required:—

(1) *Ammonium Molybdate*.—Dissolve 3 grams of the powdered crystals in 100 c.c. of water.

(2) *Dilute Nitric Acid*.—Dilute 30 c.c. of the concentrated acid to 100 c.c.

(3) *A Washing Solution* containing 50 grams of ammonium nitrate and 40 c.c. of concentrated nitric acid per litre of water.

Preparation of a Solution for Analysis.—As a rule all the phosphorus can be obtained in solution by boiling the substance with concentrated nitric acid. For complex rocks containing silicates, however, fusion with sodium carbonate is necessary, and the silica must be removed by evaporation to dryness in presence of nitric acid.

The phosphorus must be in the form of ortho-phosphate; meta- or pyro-phosphates must therefore be boiled with dilute nitric acid for a few minutes.

Procedure.—Acidify the solution with nitric acid and evaporate, if necessary, to about 80 c.c. Add about 8 grams of ammonium nitrate and 10 c.c. of the nitric acid, and heat to 70°. Heat 20 c.c. of ammonium molybdate solution to 70°, and add it slowly and with constant stirring to the hot phosphate solution. Take care not to touch the side of the beaker with the stirring-rod. Stir for a few minutes. After about twenty minutes, filter through a Gooch crucible and wash with 60 to 80 c.c. of the prescribed washing solution.

Place the Gooch crucible inside a platinum crucible in which a perforated porcelain disc is first dropped. Heat the platinum crucible very carefully to dull redness until the precipitate has a uniform greenish-black colour. Weigh the phospho-molybdic anhydride obtained.

Determination of Phosphate as Magnesium Pyrophosphate.

(*Precipitation as Magnesium Ammonium Phosphate.*)

OUTLINE OF METHOD.—The phosphate is precipitated by addition of “magnesia mixture” as magnesium ammonium phosphate, which is converted by ignition into magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

Magnesium Ammonium Phosphate, MgNH_4PO_4 .—The properties of this precipitate, and the conditions under which it may be obtained pure, are described on p. 172. The precipitate has the composition corresponding to the normal salt, MgNH_4PO_4 , only when these conditions are rigidly adhered to.

Magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, has already been described (p. 172).

Procedure.—The phosphate must all be present as orthophosphate; if any pyro- or meta-salt is present, the solution must be boiled for some time with dilute nitric acid.

Add ammonia until the solution is slightly alkaline, and evaporate, if necessary, to 100 c.c. For every 0.2 gram of P_2O_5 present (or believed to be present), add 15 c.c. of magnesia mixture (p. 207). The magnesia mixture must be added rapidly, with constant stirring.

The precipitate should separate slowly and appear crystalline. After about twenty minutes, add 25 c.c. of 2N ammonia, and set aside for at least four hours before

filtration. Filter, and wash with dilute ammonia (see p. 173) until the washings are free from chloride.

If the original phosphate solution contains much ammonium chloride, precipitate with magnesia mixture as described, and set aside for at least twelve hours. Decant the liquid through a filter, and dissolve the precipitate—which has been retained in the beaker—in the minimum quantity of dilute hydrochloric acid. Add a few drops of magnesia mixture, and reprecipitate the phosphate by adding ammonia, drop by drop, until present in decided excess. Filter after about four hours, using the original filter paper.

Dry, ignite, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. For details of this part of the procedure, see p. 173.

POTASSIUM AND SODIUM.

Potassium and sodium usually occur together. Potassium may be determined without determining sodium, but the determination of sodium involves that of potassium. In order to determine both potassium and sodium, all other metals must be removed and the residual solution evaporated to dryness. The residue is completely converted into chloride, and weighed. The amount of potassium in the mixed salts is then ascertained by one or other of the methods given below, and the sodium found by difference. For details, see p. 250.

The determination of sodium and potassium in an insoluble silicate is described on p. 289.

Forms in which Potassium is precipitated.

Potassium Chloroplatinate.—Ammonium salts and all metals other than sodium and potassium must be removed. Sulphate and phosphate must also be removed.

Potassium Perchlorate.—The special advantages of this method are that the use of expensive platinum salts is avoided, and that it is applicable in presence of phosphate and of most metals. The only common acidic radical that

must be removed is sulphate. Ammonium salts must be removed.

Dipotassium Sodium Cobaltinitrite.—This method is sometimes useful because it is applicable in presence of sulphate. Ammonium salts must be removed.

Preparation of a Solution for Analysis.

(1) *In the Complete Analysis of a Mixture*, all other metals are removed prior to the determination of sodium and potassium. If any sulphate or phosphate is present, add barium hydroxide solution in slight excess and, without filtration, evaporate to about 50 c.c. Add a few drops of freshly prepared ammonium carbonate solution in order to precipitate the barium salt, filter through a small filter paper, and wash with hot water. Determine the sodium and potassium in the filtrate.

(2) *If only Potassium is to be determined*, extract a weighed sample of the original material with hot, dilute hydrochloric acid, and filter from any insoluble matter. (With many minerals, particularly silicates, it is not possible to bring the potassium into solution by treatment with hydrochloric acid. The procedure for a case of this kind is described on p. 289.) Evaporate the solution of mixed chlorides to dryness in a porcelain basin, and heat on a sand-bath to barely-visible redness for about fifteen minutes, in order to convert iron, aluminium, etc., into insoluble basic salts. The duration of the ignition should be such that, on extracting the residue with water, a colourless solution, free from iron, is obtained.

When sulphate is present, it must be removed (except for the cobaltinitrite method) after the evaporation to dryness by adding a slight excess of barium hydroxide solution, and completing the evaporation and ignition as described above.

Extract the soluble alkali salts by repeated treatment with boiling water, breaking up the insoluble residue as much as possible with a glass rod. Filter into a glass evaporating basin, and determine the potassium by the perchlorate method.

Determination of Potassium as Chloroplatinate.

OUTLINE OF METHOD.—After removal of sulphate, phosphate, ammonium salts, and all metals other than sodium and potassium, hydrochloroplatinic acid is added, and the solution is evaporated to dryness. The residue is extracted with methyl alcohol, which dissolves the sodium chloroplatinate. The insoluble residue of potassium chloroplatinate is dried and weighed.

Potassium Chloroplatinate, K_2PtCl_6 , is a golden-yellow, crystalline salt. It is sparingly soluble in water, and nearly insoluble in methyl alcohol and in ethyl alcohol. At 20° , 100 grams of each of these solvents, in the order named, dissolves 0.77 gram, 2.7 mgrms., and 1 mgrm. The precipitate obtained in quantitative analysis is, after washing and drying, not pure K_2PtCl_6 ; it is, however, of constant composition, if the working conditions are always the same. By adopting the procedure described below, the precipitate contains 16.03 per cent. of potassium (calculated for K_2PtCl_6 , $K = 16.09$ per cent.).

As ammonium chloroplatinate is also insoluble in alcohol, it is essential to remove all ammonium salts prior to the precipitation, and also to guard against contamination of the solution by ammonia from the laboratory atmosphere during the analysis.

Sodium Chloroplatinate, $Na_2PtCl_6 \cdot 6H_2O$, is an orange-red salt which is soluble in absolute ethyl alcohol, somewhat more soluble in absolute methyl alcohol, and readily soluble in water. The hydrated salt becomes anhydrous at the temperature of the steam-bath. The anhydrous salt is less soluble in absolute alcohol than the hydrated salt. In order to separate sodium and potassium chloroplatinates, it is best to use absolute *methyl* alcohol.

Procedure.—The solution, after removal of sulphate, phosphate, and all metals other than sodium and potassium, is evaporated to dryness. The sodium and potassium are obtained finally in a platinum crucible as pure chlorides, and weighed. Full details of the procedure up to this stage are given on p. 251. The potassium is then determined as chloroplatinate, as follows:—

Dissolve the mixed chlorides in 5 c.c. of water and transfer the solution, with the rinsings of the crucible, to a small porcelain basin.

Both the sodium and potassium chlorides must be converted into chloroplatinates, because sodium chloride is insoluble in alcohol. In order to calculate the amount of hydrochloroplatinic acid required to effect this, the assumption is made that the whole of the chloride is *sodium* chloride. Since the reagent contains 10 per cent. of platinum (see p. 418), 1.7 c.c. is required for 0.1 gram of sodium chloride, and the volume of reagent required is found by multiplying the weight of the mixed chlorides by 17.

To the solution of the mixed chlorides add 0.3 c.c. more than the calculated quantity of hydrochloroplatinic acid, and place the basin on the steam-bath. Add more water, if necessary, to dissolve any precipitated potassium chloroplatinate that may remain after the solution has become warm. Evaporate until the liquid is syrupy and becomes solid on cooling.

Add about 5 c.c. of absolute methyl alcohol to the residue and break up the mass thoroughly with a platinum spatula or glass rod. Decant the liquid through a Gooch crucible that has been dried at 160° and weighed. The solid must be kept as far as possible in the basin, only the clear liquid being poured into the filter. Repeat this treatment with successive *small* quantities of methyl alcohol (grinding up the precipitate each time as thoroughly as possible) until the filtrate is colourless, and until no orange-red particles of the sodium salt can be seen amongst the golden-yellow potassium chloroplatinate. Transfer the precipitate to the Gooch crucible. Wash the sides of the crucible five or six times with small quantities of alcohol, drain off the alcohol thoroughly, dry at 160°, and weigh.

The weight of the precipitate multiplied by 0.1603 gives the weight of potassium, and multiplied by 0.3058 gives the weight of potassium chloride.

Determination of Potassium as Perchlorate.

OUTLINE OF METHOD.—The solution of mixed chlorides is evaporated almost to dryness with perchloric acid. All salts other than potassium perchlorate are then extracted with alcohol, and the insoluble residue is weighed.

Potassium Perchlorate, KClO_4 , is a sparingly soluble, crystalline salt. At 25° , 100 grams of water dissolves 2.08 grams of the salt, 100 grams of 99 per cent. alcohol dissolves 19 mgrms., and 100 grams of 98 per cent. alcohol containing 0.2 per cent. of perchloric acid dissolves 10 mgrms. The solubility decreases rapidly with falling temperature, and 100 grams of the last named solvent at 10° dissolves only about 3 mgrms. The salt may be dried without decomposition above 100° and below 200° .

Sodium Perchlorate is a white salt which is readily soluble in water and alcohol.

Procedure.—To the solution of the mixed potassium and sodium chlorides, add 10 c.c. of 20 per cent. perchloric acid.¹ (If the mixed chlorides weigh less than 0.2 gram, 5 c.c. may be sufficient.) Evaporate the solution, in a quartz or “resistance” glass basin, *almost* to dryness. The evaporation is performed on a sand-bath or, preferably, on a shallow sand-bath tray covered with a set of rings. Add another 5 c.c. of perchloric acid and again evaporate practically to dryness. If copious evolution of perchloric acid (white fumes) is not observed towards the end of the evaporation, more acid must be added and the evaporation repeated. (The amount of perchloric acid used must be more than sufficient to convert all the salts into perchlorates.)

Prepare two washing solutions as follows:—(A) Add 0.3 c.c. of 60 per cent. perchloric acid to 100 c.c. of “absolute” alcohol; for this solution make a special “wash-bottle” from an ordinary test-tube—the outlet tube and *fine* jet being made from a single piece of glass tubing. (B) Saturate 100 c.c. of rectified spirit with potassium perchlorate; the alcohol and perchlorate crystals must be vigorously shaken in a stoppered bottle for several minutes immediately before decanting or filtering a portion for use.

¹ Perchloric acid (60 per cent.), free from potassium salts, is obtainable commercially.

Prepare a Gooch-crucible filter—using somewhat more asbestos than usual—and fit the adapter into a filter-tube (a test-tube with side-tube) instead of the usual filter-flask.

To the almost dry, *cold* residue add 10 c.c. of washing solution (*A*), stir well with a flat-ended glass rod and set aside for about five minutes with occasional stirring. Allow the potassium perchlorate to settle, and decant through the Gooch crucible. (Reject the filtrate.)

Dissolve the perchlorate in the minimum amount of hot water,¹ and evaporate to dryness on the steam-bath. *Cool thoroughly*, add 10 c.c. of washing solution (*A*), stir, and decant through the filter. Transfer the perchlorate to the crucible with the minimum amount (10 to 20 c.c.) of the washing solution. Remove with a feather (p. 28) the perchlorate adhering to the side of the basin; this requires special care because it is not easily seen while the basin is wet. Finally, wash the filter five or six times by running into it from a small pipette successive portions (3 c.c.) of washing solution (*B*). The total volume of the filtrate (excluding the initial 10 c.c. rejected) should not exceed 40 to 50 c.c.

Dry for one hour at 130° to 150°, cool, and weigh. Wash again with 2 to 3 c.c. of washing solution (*B*), dry, and weigh.

Determination of Potassium as Dipotassium Monosodium Cobaltinitrite.

OUTLINE OF METHOD.—The solution containing potassium and sodium chlorides (nitrates or sulphates) is evaporated to dryness with an excess of sodium cobaltinitrite. The residue is extracted with acetic acid, washed with water, dried, and weighed.

Dipotassium Monosodium Cobaltinitrite,



is a lemon-yellow, crystalline salt, very sparingly soluble in water and in dilute acetic acid. The monohydrate is stable at 100°.

¹ This is omitted if sodium is absent.

The sodium cobaltinitrite reagent is prepared as follows :— Dissolve 28 grams of cobalt acetate in a mixture of 75 c.c. of water and 25 c.c. of glacial acetic acid, and add a solution of 55 grams of sodium nitrite in 100 c.c. of water. Warm the mixture gently in a round-bottomed flask and evacuate the flask to remove oxides of nitrogen. Set the solution aside for twenty-four hours. (A slight yellow precipitate invariably separates because sodium nitrite is rarely free from potassium salts.) Filter, and dilute the solution to 250 c.c. The solution should be kept in the dark.

Procedure.—To the solution of the mixed potassium and sodium salts (containing, preferably, not more than 0.1 gram of the potassium salt), add an excess of the reagent (about 5 c.c.) and evaporate to dryness on the steam-bath. After cooling, stir the residue with 5 per cent. (approximately normal) acetic acid, allow the precipitate to settle, and decant through a Gooch filter. Wash the precipitate by decantation with acetic acid, transfer it to the crucible, and wash with cold water until free from acid. Dry at 100° , and weigh as $\text{K}_2\text{NaCo}(\text{NO}_2)_6, \text{H}_2\text{O}$.

Determination of Potassium and Sodium.

OUTLINE OF METHOD.—All metals other than sodium and potassium are removed. The solution is evaporated to dryness, and the residue of mixed chlorides weighed. The potassium is then determined by either the chloroplatinate or the perchlorate method and the sodium found by difference.

Sodium Chloride is readily soluble in water but is almost insoluble in alcohol. It may be dried completely at 100° , but unless the drying process is very prolonged, it mechanically retains a trace of water which is expelled, with decrepitation, at higher temperatures. Heated to dull redness it melts, and at a bright red heat volatilises rapidly; at all temperatures above the melting-point, there is appreciable loss by volatilisation.

Potassium Chloride very closely resembles sodium chloride in properties.

Procedure.—Evaporate the solution (from which sulphate, phosphate, and all metals other than the alkalis have been

removed) in a porcelain basin until the bulk is reduced to about 50 c.c. Transfer it to a 100 c.c. platinum basin and rinse the porcelain basin with hot water. Evaporate to complete dryness on the steam-bath. (The subsequent manipulation is facilitated if the residue is dried at this stage as completely as possible, and it is advisable to heat the covered basin in an air-oven at 120° to 150° for an hour or more.)

Place the basin on a sand-bath and heat—very gently at first—until all moisture is driven off. During this operation, the basin must be kept covered with a clock-glass and the heating interrupted whenever decrepitation begins. When decrepitation has wholly ceased, raise the temperature, but do not remove the clock-glass. Continue the heating until the clock-glass and the sides of the basin are thickly coated with ammonium chloride.

Remove the clock-glass. Invert it and heat it gently over a small flame until all the ammonium chloride has volatilised, and set it aside until required later.

Place the basin on a pipe-clay triangle, and heat the sides of the basin until the ammonium chloride has volatilised. The burner must be held in the hand and the flame kept in constant motion to prevent over-heating and consequent volatilisation of any alkali chloride. Next heat the bottom of the basin in the same manner until no more ammonium chloride is given off. During this process the residue almost invariably blackens owing to the charring of traces of organic impurities from the reagents.

Cool, add about 5 c.c. of hot water, and filter through a very small ($5\frac{1}{2}$ -cm.) filter paper into a tared platinum crucible. *Extreme care is necessary at this stage, since the loss of a single drop of the solution renders the determination valueless.* Wash the basin and filter paper with hot water, using about 2 c.c. for each washing. Wash into the crucible also any trace of salt adhering to the clock-glass.

Add one drop of hydrochloric acid and evaporate to complete dryness on the steam-bath. When the residue is apparently dry, remove from the steam-bath and heat the covered crucible with a small flame, observing the same precautions as before against over-heating. Cool, and weigh.

Repeat the heating until the weight is constant. (The salt is sometimes dark in colour on account of traces of carbon. The carbon will disappear on prolonged heating, but its weight is negligible.) The weight gives the amount of potassium and sodium chlorides.

Determine the amount of potassium in the mixed chlorides by following the instructions given on p. 246 or on p. 248, according to the method employed.

Calculate the weight of potassium chloride corresponding to the weight of potassium chloroplatinate (or perchlorate) obtained. Subtract the weight of potassium chloride from that of the mixed chlorides in order to find the weight of sodium chloride.

SILICA AND SILICATES.

Properties of Silica.—From the analytical point of view, one may distinguish between three varieties of silica: (1) the jelly obtained by the incomplete dehydration of precipitated “silicic acid”; (2) silica obtained by the ignition of precipitated “silicic acid”; (3) native silica.

Gelatinous “silica” is readily soluble in alkali hydroxides and carbonates, and appreciably soluble in water and in acids. After ignition, it is practically insoluble in water and in acids (except hydrofluoric acid), but dissolves slowly in alkalis. Native crystalline silica (*e.g.* quartz) is insoluble in acids (except hydrofluoric acid), and is only slowly attacked by alkalis.

The powder obtained by drying gelatinous silica at 100° contains about 13 per cent. of water. Even at 200° , it still retains about 5 per cent.; only on ignition is the last trace of water expelled. The silica obtained by drying the jelly at 100° dissolves to an appreciable extent in acid, and is not rendered completely insoluble (as is often stated) by repeated evaporation to dryness with hydrochloric acid.

Precipitated silica is hygroscopic unless it has been ignited for at least twenty minutes with a blowpipe or a Méker burner.

Determination of Silica in an Insoluble Silicate.

OUTLINE OF METHOD.—The silicate is decomposed by fusion with sodium carbonate. The fused mass, after cooling, is disintegrated by warming with dilute hydrochloric acid, and the solution is evaporated to dryness on the steam-bath. The residue is moistened with alcohol and is again taken to complete dryness on the steam-bath. Hydrochloric acid and water are added, and the silica, most of which remains insoluble, is separated by filtration. The solution, which still contains a little silica, is evaporated to dryness again, and the residue is treated as before. The silica is then dehydrated by ignition and is weighed as SiO_2 .

Procedure.—In a small weighing-bottle place from 0.9 to 1.1 gram of the finely powdered silicate, and weigh accurately. Transfer the powder to a platinum (or palau) crucible containing about 3 grams of pure, dry sodium carbonate. (Re-weigh the weighing-bottle to find the weight of silicate taken.) Add to the crucible another 3 grams of sodium carbonate. Place the crucible on a sheet of glazed paper and mix the contents very thoroughly by stirring gently with a small spatula (preferably of platinum), care being taken that no unmixed silicate remains at the bottom of the crucible.

Cover the crucible, place it on a triangle about 4 inches above a small Bunsen flame, and heat gently for about five minutes. Then lower the crucible and increase the flame gradually so as to melt the contents without any spluttering. Cautiously lift the lid of the crucible at intervals and examine the contents to make sure that there is no excessive frothing. No spatter should be seen on the lid if the fusion has been properly conducted. After heating until a state of quiet fusion is attained, heat the crucible with a Méker burner for about fifteen minutes. When the fusion is complete, the molten mixture may not be perfectly clear, but practically no further escape of gas bubbles should be seen. The whole operation takes from thirty to forty minutes.

Now lift the crucible with platinum-tipped tongs and impart a rotary motion to the vessel as cooling proceeds. In this way, the mixture is made to solidify in a thin sheet on the side and bottom of the crucible, and its subsequent removal from the crucible is thereby facilitated. As a rule

the cold cake has a bluish-green colour owing to the presence of sodium manganate.

After the crucible has become *thoroughly cold*, half-fill it with water and warm *cautiously* with a very small flame for several minutes; this will often suffice to loosen the cake—especially from a palau crucible. Transfer the liquid and the cake to a 6-inch porcelain basin containing 150 c.c. of hot water, and carefully rinse the crucible into the basin to remove as far as possible any adhering portions of the cake. Set the crucible and lid aside for final cleaning at a later stage. If the cake cannot be readily loosened in this way, place the crucible on its side in the porcelain basin together with 150 c.c. of hot water, and warm on the steam-bath until the mass is completely detached from the crucible. Remove the crucible, rinse it carefully, and set it aside with the lid for final cleaning. Break up the cake as far as possible with a blunt glass rod and then add, very gradually, excess of hydrochloric acid (20 c.c. of concentrated acid mixed with 10 c.c. of water), the basin being covered with a clock-glass to prevent loss during the decomposition of the carbonate.

When the disintegration is complete and effervescence has ceased, remove the clock-glass. Clean the crucible and the under side of the lid with a few drops of warm hydrochloric acid and add the rinsings of both to the basin. Evaporate to dryness on the steam-bath. Towards the end of the evaporation, stir frequently in order to break the crust that forms on the surface of the liquid. When the mass is almost dry, remove the basin from the steam-bath and allow it to cool. Add 15 c.c. of alcohol and stir. Evaporate again to *complete dryness* on the steam-bath. (More complete dehydration of the silica is secured by the addition of alcohol at this stage; the silica is then almost wholly insoluble in acid and the second evaporation of the solution—indicated below—may be omitted except in analyses of the highest accuracy.)

Moisten the dry powder with 10 c.c. of concentrated hydrochloric acid, stir, and set aside for ten minutes in order that any basic salts (of iron, etc.) may be converted into normal chlorides. Then add about 30 c.c. of water and heat

on the steam-bath and stir frequently until only the silica remains undissolved. The silica is often in a coarse condition and may be ground finer with a blunt glass rod.

Filter through a 9-cm. paper. Wash the silica several times by decantation with hot dilute acid. (The acid is not put into the wash-bottle but a little is added to the basin with each portion of hot water.) Transfer the silica to the filter. Remove any silica adhering to the basin and stirring rod with a small piece of filter paper and add this to the main precipitate. Then wash the precipitate and paper with hot water until a few drops of the washings give no turbidity with silver nitrate.

Some of the silica always dissolves in the hydrochloric acid—probably only a fraction of 1 per cent. of the total silica if the above procedure was followed—and most of this may be recovered by evaporating the filtrate again to complete dryness. The residue is treated with acid, water is added, and the solution filtered through another (smaller) paper. The basin and the filter are washed with hot dilute acid and then with hot water as before.

The filter papers containing the silica are incinerated, without previous drying, in a weighed platinum crucible precisely in the manner described on p. 152. After all the carbon has been oxidised, ignite the silica in the covered crucible with the full flame of a Méker burner for at least twenty minutes. Cool, and weigh the SiO_2 . Repeat the ignition until constant weight is attained.

The silica obtained in this way is never entirely free from impurities, and it is necessary to determine the amount of impurity by driving off the silica with hydrofluoric acid and weighing the non-volatile residue. To accomplish this, moisten the silica with water, add one or two drops of concentrated sulphuric acid, and 4 to 5 c.c. of hydrofluoric acid. Evaporate to dryness, first on the steam-bath and then with a Bunsen flame (see p. 24 and Figs. 13 and 14). Ignite for two or three minutes with a Méker burner, cool, and weigh. (**Caution.**—Take great care in handling hydrofluoric acid, and carry out the evaporation in a good draught.)

Pure silica should leave no residue, and the weight of the impurity must therefore be subtracted from the weight of

the crude silica. The residue usually contains oxides of aluminium, iron, titanium, and phosphorus, and it may weigh from 2 to 10 mgrms. If a complete analysis of the silicate is being made, the subsequent precipitate of alumina, etc., should be ignited in the crucible containing the impurity found in the silica.

Notes.—(1) The evaporations for the removal of silica must be continued until the residue forms a *dry powder*. This powder is often very light, and, like ignited silica, is very easily blown away if care is not taken to protect it from draughts.

(2) In accurate work, the weight of the crude silica should always be corrected for impurity. If, however, it is not intended to determine the silica which, in spite of all the precautions described above, escapes precipitation and is found along with the ferric oxide and alumina (see p. 288), the correction should not be applied; instead, the assumption is made that the weight of the impurity is equal to that of the silica which has passed into the filtrate.

(3) The hydrofluoric acid must be free from non-volatile impurities. The acid supplied in ceresine bottles is usually pure, but it is advisable to test a sample. A correction must be applied if there is any non-volatile residue.

“Silica” as an Insoluble Residue.

In many minerals, slags, and technical products, the residue left after treatment with acid is mainly silica. It is often permissible, *e.g.* in analyses made for technical purposes, to report the insoluble residue, without further examination, as “silica” or “silica and insoluble silicates.” Typical examples of the determination of “silica,” where “silica” means the only portion insoluble in acid, are described under Dolomite (p. 281) and Pyrites (p. 295). In these determinations some of the silica usually dissolves; but, on the other hand, the residue is not entirely silica, and for many purposes the uncorrected results are sufficiently accurate.

When an accurate determination of the silica is required, the following modifications are necessary:—(1) The “silica” must be evaporated with hydrofluoric and sulphuric acids

and the weight of the non-volatile residue ascertained (p. 255). (2) The residue from the "silica" must be fused with sodium carbonate and added to the main solution. (3) The solution must be evaporated to complete dryness and the silica separated in the manner already described (p. 254).

SILVER.

The volumetric method for the determination of silver, described on p. 130, is convenient and accurate.

Gravimetrically, silver is usually determined as chloride, but the gravimetric determination as silver bromide may be recommended.

Forms in which Silver is precipitated.

Silver Chloride.—Silver may be determined by this method in presence of all other metals. The silver is precipitated with dilute hydrochloric acid, carefully avoiding unnecessary excess. If a mercurous salt is present, it must be oxidised with concentrated nitric acid prior to the precipitation of the silver. If lead is present, the solution must be diluted and the hydrochloric acid added very slowly. Otherwise the procedure is identical with that adopted in determining chloride as silver chloride (p. 164).

Silver Bromide.—This method is preferable to the chloride method on account of the lower solubility of silver bromide. The solution is acidified with nitric acid and potassium bromide added until precipitation is complete. The procedure is otherwise identical with the previous method. For the properties of silver bromide, see p. 213.

SODIUM (see p. 244).

SULPHATE.

There is no convenient volumetric method for the determination of sulphate.

Sulphate is always determined gravimetrically as barium sulphate. For details, see p. 169.

SULPHIDE.

A volumetric method for the determination of hydrogen sulphide is described on p. 112. Many sulphides are readily decomposed by dilute acids, and the volumetric method may therefore be adapted to their determination.

In order to determine sulphide gravimetrically, a weighed sample (or measured volume) is decomposed with hydrochloric acid in an apparatus similar to that shown in Fig. 36, p. 114. To prevent liberation of sulphur by atmospheric oxidation, the apparatus must be filled with carbon dioxide or hydrogen. The hydrogen sulphide is led into a solution of ammonia and hydrogen peroxide, and is thereby oxidised to sulphate. The sulphate is determined in the usual manner as barium sulphate.

The oxidation of the hydrogen sulphide may also be effected by absorbing the gas in sodium hydroxide solution, and then adding bromine.

The determination of sulphur in mineral sulphides is described in connection with the analysis of Iron Pyrites (p. 295), Copper Pyrites (p. 297), and Zinc Blende (p. 300).

TIN.

Tin is a constituent of many alloys, such as solder, type metal, bearing (anti-friction) metal, bronze, etc. Apart from its occurrence in alloys, it is rarely met with in analysis except as cassiterite, which is mainly stannic oxide.

The determination of tin is best accomplished by volumetric methods which are far more reliable than any gravimetric method. The latter are usually troublesome and are often inaccurate, more especially when the determination involves the separation of the tin from antimony, arsenic, lead, and copper, with which it is commonly associated. The volumetric method described on p. 118 is applicable to tin alloys and ores containing also antimony, arsenic, lead, and copper.

A concise account of the most reliable and rapid methods for the determination of tin in its ores and alloys is given in Parry's *The Assay of Tin and Antimony*.

Forms in which Tin is precipitated.

Stannic Acid.—When a tin alloy is disintegrated with nitric acid, the tin is converted into insoluble stannic acid which may be ignited and weighed as stannic oxide. This method may be used without serious error for alloys such as brass containing less than 2 per cent. of tin, but it is inaccurate in the case of alloys that are richer in tin unless the stannic oxide is examined for traces of other oxides which are pertinaciously retained by it. The method is not applicable to alloys containing antimony, arsenic, or phosphorus.

Stannic Sulphide.—Tin is completely precipitated in this form by hydrogen sulphide in presence of hydrochloric acid the concentration of which is not higher than 2N. The precipitate may be oxidised by ignition in air and the stannic oxide weighed; or it may be dissolved in hydrochloric acid (with addition of potassium chlorate) and the tin in solution determined volumetrically.

Stannic sulphide is not precipitated from a solution containing 15 per cent. of hydrochloric acid (about 4N) or an excess of oxalic acid (compare antimony sulphide, p. 206).

TITANIUM.

At one time regarded as a comparatively rare element, titanium is now recognised as one of the most widely distributed and is more abundant in actual amount in the earth's crust than many more familiar elements such as tin, lead, carbon, and sulphur. It is probably an invariable constituent of all silicate rocks, although usually present to the extent of only 1 per cent. or less, but seldom merely as traces. It is also met with as an alloy in ferro-titanium, and is sometimes present in cast-iron and steel.

Titanium is precipitated by ammonia (or in the basic acetate method described under aluminium on p. 203) as meta-titanic acid, $\text{TiO}(\text{OH})_2$, and in rock analysis is separated in this form together with the hydroxides and phosphates of iron and aluminium. The mixed precipitate, which after ignition contains the titanium as TiO_2 , is brought into solution after fusion with potassium pyrosulphate (p. 287), and the titanium is determined colorimetrically (p. 194).

WATER.

Three methods, with many modifications of each, are used for the determination of water. The accuracy of the determination often depends on the choice of the appropriate method.

(1) **Indirect Method.**—A weighed sample is heated to a high temperature and the loss of weight is determined. This method is not always applicable.

(2) **Direct Method.**—A weighed sample is heated and the water evolved is collected and weighed. There are many modifications of the method of heating the substance and of collecting the water. The direct method is more generally applicable than the indirect method, but is somewhat more troublesome.

(3) **Carbide Method.**—A weighed sample is intimately mixed with calcium carbide and the liberated acetylene is measured. The application of heat may or may not be necessary.

A modification of this method consists in determining the loss of weight when weighed quantities of the substance and of calcium carbide are mixed. For details, see papers by F. H. Campbell (*J. Soc. Chem. Industry*, 1913, **32**, 67, where a full list of references to other modifications is given), and Huntly and Coste (*J. Soc. Chem. Industry*, 1913, **32**, 61).

Indirect Determination of Water.

As this is the easiest method, it is used whenever possible. It is inaccurate—

- (1) If anything except water is lost during the dehydration. This is particularly liable to occur with carbonates, organic substances, and ammonium compounds.
- (2) If the substance is readily oxidised. The method therefore gives inaccurate results if, for example, ferrous salts are present.

The first error can be avoided in some cases by dehydrating at a low temperature by means of a current of dry air or in a vacuum. The second error is avoided by dehydrating in an oxygen-free atmosphere or in a vacuum.

Three of the many modifications of the indirect method may be mentioned :—

(1) Gentle ignition until constant weight is attained. The procedure has already been described for the determination of water in magnesium sulphate heptahydrate (p. 156).

(2) Drying in a steam-oven or hot air-oven at constant temperature. Most hydrated salts can be dried at temperatures between 100° and 200° without further decomposition. There is no fixed temperature at which hydrated salts will become anhydrous, and it is therefore necessary to find by trial the temperature, if any, at which the water can be expelled without further decomposition of the substance.

The substance is weighed in a wide, shallow weighing-bottle, and the open bottle is placed in the hot air-oven for one hour. The bottle is then removed and cooled in a desiccator. The stopper must be replaced before weighing, as reabsorption of moisture may occur. The procedure is repeated until the weight is constant.

(3) Most substances may be dried without decomposition in a vacuum desiccator containing sulphuric acid or fused calcium chloride. The substance should be weighed in a wide, shallow bottle or on a watch-glass. Dehydration may proceed so slowly at the ordinary temperature that it becomes complete only after many days; if the substance is heated in vacuo, dehydration takes place very quickly and there is no risk of oxidation.

Direct Determination of Water in a Mineral.

If the mineral on ignition loses only water and carbon dioxide, the following simple method (Brush and Penfield's) is convenient and accurate.

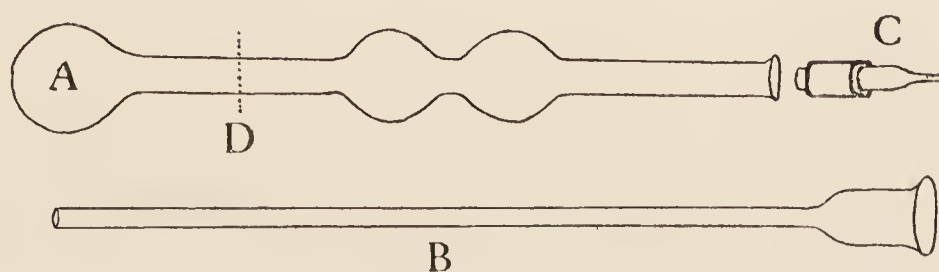


FIG. 66.

The mineral is heated in a hard-glass tube (about 20 cm. long and 5 mm. in diameter), which is enlarged into a bulb A (Fig. 66) at the closed end. One or more bulbs are provided

near the middle of the tube in order to catch the water and prevent it running back and cracking the hot glass. A stopper C, for the open end of the tube, is made from a piece of tubing drawn out to a capillary and fitted with rubber tubing.

Even if apparently dry, these tubes must be thoroughly dried before use, by heating and blowing air through them by means of a narrow glass tube reaching to the bottom.

Procedure.—Weigh the empty bulb-tube. Introduce, by means of the tube B, from 0.5 to 1 gram of the substance, and weigh again. Insert the stopper C and clamp the tube in a horizontal position. Wrap strips of wet filter paper round the middle bulbs. Heat the bulb A gently at first and then more strongly, with a Bunsen or a Méker burner, according to the temperature required to expel the water. It is advisable to protect the middle bulbs from the heat of the flame by means of a piece of asbestos board placed near the point D.

When the water has been completely expelled, draw off the heated end of the tube in a small blow-pipe flame at the point D. Clean and dry the tube externally, cool for half an hour, and weigh it (without the stopper). Remove the water by warming the tube and aspirating air through it. Weigh the tube again after cooling.

If the substance contains sulphur, fluorine, etc., it must be mixed with a suitable "retainer," such as calcium oxide (see *Amer. Journ. Sci.*, 3rd series, **48**, 31, 1894).

Exercise.—Determine the percentage of water in gypsum or in barium chloride, heating with a Bunsen flame only.

ZINC.

The volumetric method for the determination of zinc (p. 136) is more expeditious than the gravimetric methods, and is capable of yielding excellent results. The method requires practice, however.

Zinc is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. Zinc sulphide is partially precipitated with the sulphides of the copper group unless the solution is very strongly acid, and, in

order to effect a complete separation, it may be necessary to redissolve the copper group precipitate, after filtration, and to reprecipitate with hydrogen sulphide.

Forms in which Zinc is precipitated.

Basic Zinc Carbonate.—This method is applicable only when all metals other than sodium and potassium are absent. It is inaccurate in presence of ammonium salts, but these can be removed before precipitation. For details, see p. 168.

Zinc Ammonium Phosphate.—This method is available in presence of sodium, potassium, and ammonium salts only.

Zinc Sulphide.—Zinc may be separated from the calcium group by precipitation as sulphide, and in general analysis this is frequently the only available method. As, however, it is a matter of considerable difficulty to obtain zinc sulphide in a form suitable for filtration, it is preferable, when circumstances permit, to precipitate as basic carbonate or as phosphate.

A complete separation of zinc from iron, aluminium, manganese, cobalt, and nickel is obtained by precipitation as sulphide in presence of formic acid.

Determination of Zinc as Phosphate.

OUTLINE OF METHOD.—The zinc is precipitated as zinc ammonium phosphate by means of ammonium phosphate in neutral or very faintly acid solution. It is weighed either as $\text{Zn}(\text{NH}_4)\text{PO}_4$ after drying at 120° , or as $\text{Zn}_2\text{P}_2\text{O}_7$ after ignition.

Zinc Ammonium Phosphate is a white, crystalline powder, insoluble in water and in solutions of ammonium salts, but somewhat soluble in ammonia. It is readily soluble in mineral acids, but is almost insoluble in very dilute acetic acid. It may be dried without decomposition at temperatures not exceeding 140° ; heated above 200° , it is converted into zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$.

Zinc Pyrophosphate is a white powder which may be heated to dull redness without decomposition. Flame gases and carbonaceous matter must be carefully excluded during the ignition, otherwise reduction and volatilisation will occur.

Procedure (In absence of sodium and potassium).—Evaporate the solution to 100 c.c., cool, add 5 grams of

ammonium phosphate (the di-ammonium salt) dissolved in water, and then add ammonia until the solution is neutral (test with litmus paper). Add 1 c.c. of dilute acetic acid, and stir. Heat on the steam-bath for an hour; in that time the precipitate should be crystalline and should have settled completely. Filter through a Gooch crucible, wash with hot water, dry at 110° to 120° , and weigh as $\text{Zn}(\text{NH}_4)\text{PO}_4$.

The above method is accurate, but if it is desired to weigh as pyrophosphate, the Gooch crucible must be placed inside a platinum or nickel crucible and ignited—at first gently, but finally to redness. Care must be taken to exclude flame gases during the ignition, since reduction (with volatilisation of the zinc) occurs readily.

Note.—The above mentioned conditions of acidity during the precipitation must be rigidly adhered to, otherwise precipitation is incomplete.

Modification if Alkalis are present.—If sodium or potassium salts are present, even in small amount, the precipitate obtained is a mixture of zinc ammonium phosphate and zinc potassium (or sodium) phosphate.

When these salts are present, add 20 grams of ammonium chloride to the solution and precipitate as described above. When the precipitate has settled, decant through a Gooch crucible and wash three times with hot water by decantation, care being taken that as little as possible of the precipitate is washed into the crucible.

Dissolve the precipitate in the beaker in the minimum amount of dilute hydrochloric acid, add 10 grams of ammonium chloride, and repeat the process of neutralisation and precipitation. Filter through the Gooch crucible used in the first operation, wash thoroughly, ignite, and weigh as $\text{Zn}_2\text{P}_2\text{O}_7$.

It is necessary in this case to ignite to pyrophosphate, as in presence of large amounts of ammonium salts, the zinc ammonium phosphate is contaminated with ammonium salts which are not completely removed by washing.

If only sodium salts are present, a single precipitation in presence of a large amount of ammonium chloride is sufficient. The precipitate must be converted into pyrophosphate.

Determination of Zinc as Sulphide.

(Precipitation in presence of Formic Acid.)

OUTLINE of METHOD.—The zinc is precipitated as sulphide by hydrogen sulphide in presence of a small amount of formic acid. The sulphide is converted into oxide by ignition in air and the ZnO weighed ; or it may be ignited in hydrogen and weighed as ZnS.

Zinc Sulphide, obtained by precipitation, is a hydrated, gelatinous substance. It is readily soluble in strong acids, insoluble in ammonia and in alkaline solutions generally, and almost insoluble in dilute solutions of acetic or formic acids. Whatever the conditions of precipitation, it is somewhat difficult to filter. The best precipitate is obtained from an acid solution ; it then filters fairly readily, but if washed with water, becomes more gelatinous and chokes the filter paper. It can, however, be washed with dilute solutions of ammonium salts.

Zinc sulphide is quickly oxidised to zinc oxide on ignition in air, and is therefore usually converted into oxide for weighing ; it can, however, be dried and obtained as anhydrous ZnS by gentle ignition with sulphur in an atmosphere of hydrogen, using a Rose crucible.

Zinc Oxide.—The properties of zinc oxide are described on p. 168.

Procedure.—To the zinc solution contained in a 400 c.c. conical flask, add 1 c.c. of methyl orange, and then run in carefully a dilute solution of sodium hydroxide until the last tinge of pink is discharged (avoid excess). Dilute 5 c.c. of ordinary 95 per cent. formic acid to 100 c.c., and add this to the zinc solution until a faint permanent pink colour is obtained, and then add an additional 5 c.c. of the 5 per cent. formic acid.

Dilute the solution to about 250 c.c., heat to 80°, and saturate with hydrogen sulphide under slight pressure. Pressure a little above atmospheric is readily obtained with an ordinary Kipp apparatus if the flask is fitted with a rubber cork (Fig. 67). The cork is inserted firmly into place after the air in the flask has been displaced by hydrogen sulphide. When the solution is saturated and the precipitate has

settled, the cork is removed before the apparatus is disconnected elsewhere.

Decant, filter with slight suction, and wash with a saturated hydrogen sulphide solution containing 2 per cent. of ammonium acetate; wash finally with hot water.

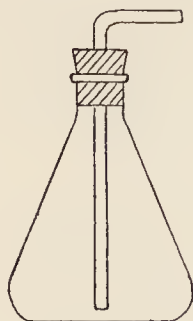


FIG. 67.

Dry the precipitate and filter paper thoroughly. Remove the precipitate as completely as possible from the filter paper, but do not rub off any paper fluff, since this would cause reduction and loss of zinc in the subsequent ignition.

If the sulphide is to be weighed, incinerate the paper in a Rose crucible before adding the precipitate. Add a little pure sulphur, ignite at a low red heat in a current of hydrogen, and weigh the ZnS .

If the sulphide is to be converted into oxide, incinerate the paper before adding the precipitate, and ignite in an open crucible with careful exclusion of flame gases. Weigh the ZnO .

PART VI

THE ANALYSIS OF SIMPLE ORES AND ALLOYS

WHEN a complete analysis of a substance is made, as in some of the examples described in this section, the sum of the ascertained percentages of the various constituents ought to be 100.0, if there were no experimental errors. In actual practice, this summation may be considered satisfactory if it lies between 99.5 and 100.5, and the results of a complete analysis ought always to be tested in this way. A satisfactory summation is, however, no proof that the analysis is accurate, since a plus error in the percentage of one constituent may balance a minus error in that of another. A summation that falls short of 100 may be due to mechanical losses (spilling of drops, spirting, etc.), or to the slight solubility of precipitates, etc.; or it may indicate that the substance contains other undetermined constituents. Errors due to imperfect washing of precipitates, impurities in reagents, the action of solutions on glass, etc., may account for a summation exceeding 100.

Examples of typical analyses are given in the Appendix (p. 420).

ANALYSIS OF A SILVER COIN.

(Alloy of Silver, Copper, and Nickel.)

Silver coins minted prior to 1920 contained, as a rule, from 90 to 95 per cent. of silver, the remainder being copper. British silver coins are now made from an alloy of silver, copper, and nickel, and the following method of analysis is applicable to an alloy of these metals.

OUTLINE OF METHOD.—The coin is dissolved in nitric acid. The *silver* is precipitated as silver chloride which is separated by filtration, dried, and weighed. In the filtrate, the *copper* is

precipitated as cupric sulphide which is converted into cuprous sulphide and weighed. After removal of copper, the *nickel* is precipitated as nickelic hydroxide which is converted into metallic nickel and weighed; or, the nickel may be determined by the diacetyldioxime method.

Procedure.

Clean the coin with emery cloth, and cut it into pieces with shears. Place a weighed portion (0.8 to 1 gram)¹ of the alloy in a 400 c.c. beaker provided with a cover-glass. Add a mixture of 10 c.c. of concentrated nitric acid and 5 c.c. of water, and warm on a hot-plate or a steam-bath until solution is complete. Rinse and remove the cover-glass, and evaporate nearly to dryness on the steam-bath.

Determination of Silver.—Dilute the solution to about 100 c.c., and determine the silver as silver chloride. Details of the procedure are given on pp. 257 and 164.

Determination of Copper.—Transfer the filtrate and washings from the silver chloride precipitation to a porcelain basin, and evaporate to dryness on the steam-bath. Add 10 c.c. of concentrated sulphuric acid, and heat the basin on a sand-bath until white fumes of sulphuric acid are copiously evolved. (This operation is necessary in order to remove nitric acid.) Allow the basin to cool, add a little water cautiously, and warm until the copper and nickel sulphates are dissolved. Transfer the solution to a 300 c.c. conical flask, dilute to 150 c.c., and determine the copper as cuprous sulphide (p. 174). Use an 11-cm. paper for the filtration.

Determination of Nickel.—Transfer the filtrate and washings to a porcelain basin and evaporate on the steam-bath as far as possible, and then heat on a sand-bath until most of the sulphuric acid is volatilised. Allow to cool, add a little water cautiously, and dilute to 100 c.c. Determine the nickel as described on p. 239, or on p. 240.

Note.—Silver coins often contain a trace of iron which may be determined (after removal of the copper) by following in detail the procedure given on p. 270 for the determination of iron in a nickel coin.

¹ If the nickel is to be determined by the diacetyldioxime method (p. 240), only 0.4 to 0.5 gram should be taken.

ANALYSIS OF A “NICKEL” COIN.

(*Alloy of Copper and Nickel.*)

“Nickel” coins are usually made of an alloy containing about three parts of copper and one part of nickel, together with traces of iron and lead. The determination of copper and nickel in the alloy may be carried out as described in the latter part of the analysis of a silver coin (p. 268), or by electrolytic methods (p. 186). The following method of analysis includes the determination of the minor constituents.

OUTLINE OF METHOD.—The alloy is dissolved in nitric acid. The solution is evaporated with sulphuric acid until all the nitric acid is expelled. The solution is diluted and any lead sulphate is separated by filtration. The *lead* is determined colorimetrically. In the filtrate the *copper* is precipitated by hydrogen sulphide and weighed as cuprous sulphide. After removal of copper, the *iron* is precipitated by ammonia and is determined volumetrically or colorimetrically. In the filtrate, *nickel* is determined by the diacetyl-dioxime method. *Lead* may be determined in a separate portion of the alloy.

Procedure.

Clean a 5- or 10-pfennig piece with emery cloth, and cut it into small pieces with shears, or roll it into a thin sheet. Place a weighed portion (0.25 to 0.3 gram) in a porcelain basin, add 2 c.c. of water and 5 c.c. of concentrated nitric acid, cover the basin with a clock-glass, and warm gently until the alloy has dissolved. Rinse and remove the cover-glass, and evaporate to dryness on the steam-bath. Add 2 c.c. of concentrated sulphuric acid, and heat carefully on a sand-bath until copious white fumes of sulphuric acid are evolved. Allow to cool; cautiously add 40 c.c. of water and stir to dissolve the copper and nickel sulphates.

Determination of Lead.—The amount of lead in 0.3 gram of the alloy is usually very small. If any insoluble lead sulphate can be seen, filter through a very small paper and wash with dilute (normal) sulphuric acid. Place the filter paper together with the precipitate in a small beaker, add about 20 c.c. of 20 per cent. ammonium acetate solution, and warm for several minutes. Filter, and wash with hot ammonium acetate solution. Determine the lead in solution colorimetrically (p. 198).

Determination of Copper.—Transfer the solution (after filtration from any lead sulphate) to a 300 c.c. conical flask, add 10 c.c. of concentrated sulphuric acid, and dilute to 100 c.c. Determine the copper as cuprous sulphide (p. 174). Use an 11-cm. paper for the filtration.

Determination of Iron.—Transfer the filtrate to a porcelain basin and evaporate on the steam-bath as far as possible. Add 1 c.c. of concentrated nitric acid (to oxidise ferrous salt) and then heat on a sand-bath until most of the sulphuric acid is volatilised. Allow to cool, and dilute to 30 c.c. Add ammonia in slight excess and boil. Filter through a small paper and wash the ferric hydroxide with a little hot water. Set the filtrate aside. Dissolve the precipitate by pouring 10 c.c. of hot, dilute hydrochloric acid into the filter and receive the solution in the original beaker. Wash the filter paper. Add about 2 grams of ammonium chloride and reprecipitate the ferric hydroxide with ammonia. Filter through the same paper and wash thoroughly. Dissolve the precipitate in 10 c.c. of dilute hydrochloric acid, wash the filter, and titrate the solution with standard titanous chloride (p. 136); or, dilute the solution to 100 c.c. in a standard flask and determine the iron colorimetrically (p. 192).

Determination of Nickel.—Mix the two filtrates from the iron precipitation and determine the nickel by the diacetyldioxime method (p. 240).

Determination of Lead (*in a separate portion*).—In a covered porcelain basin dissolve a weighed portion (about 2 grams) of the alloy by warming with a mixture of 15 c.c. of concentrated nitric acid and 15 c.c. of water. Add 5 c.c. of concentrated sulphuric acid, and proceed as described on p. 231.

Alternative Method.

The alloy may be analysed by determining the copper volumetrically in one portion, and the nickel in another portion by the diacetyldioxime method.

Copper.—In a conical flask dissolve about 0.8 gram of the alloy by gently warming with a mixture of 5 c.c. of concentrated nitric acid and 5 c.c. of water. Dilute the solution with 20 c.c. of water and boil briskly for two minutes. Add 0.5 gram of urea to destroy nitrous acid,

then add ammonia until alkaline and acidify with acetic acid. Cool, and dilute to 100 c.c. in a standard flask. Determine the copper in 25 c.c. by means of decinormal sodium thiosulphate that has been standardised with pure copper (p. 110).

Nickel.—Dissolve 0.15 to 0.2 gram in nitric acid and dilute the solution to 200 c.c. in a 400 c.c. beaker. Add a few crystals of tartaric acid (to prevent subsequent precipitation of iron as ferric hydroxide), and then add ammonia until a deep-blue solution is obtained. As described on p. 240, precipitate the nickel with diacetyldioxime (use 25 c.c. of the reagent). Filter through an 11-cm. paper, and wash the precipitate with hot water containing a little ammonium nitrate. (Reject the filtrate.) Dissolve the precipitate (which is not quite free from copper) by pouring boiling nitric acid (5 c.c. of concentrated acid mixed with 15 c.c. of water) in small portions into the filter, and receive the solution in the original beaker. Wash the filter paper with hot water. Dilute the solution to 150 c.c., add ammonia until alkaline (about 5 c.c. of concentrated ammonia diluted with a little water will be required), and reprecipitate the nickel with diacetyldioxime. Filter through a Gooch crucible, wash with hot water, dry at 120°, and weigh.

ANALYSIS OF SOLDER.

Commercial solder consists essentially of lead and tin (from 30 to 60 per cent. of the latter), but it usually contains also from 1 to 3 per cent. of antimony. When such an alloy is disintegrated with nitric acid, the insoluble residue consists of stannic and antimonie acids, together with a small amount of lead oxide. The analysis of solder by the first method described below is therefore inaccurate since the presence of antimony is ignored, but the method may be used for a pure lead-tin alloy without very serious error. The second method is capable of giving accurate results with any lead-tin-antimony alloy, such as type metal.

OUTLINE OF FIRST METHOD.—The alloy is disintegrated with nitric acid which dissolves the lead and converts the tin into insoluble stannic acid. The stannic acid is separated by filtration, ignited, and weighed as stannic oxide. The lead in solution is determined as chromate or sulphate.

Procedure.—Roll the alloy into a thin foil, or obtain filings by rubbing it on a clean, medium-cut file. Place a weighed portion (about 0.3 gram) in a porcelain basin, add 5 c.c. of concentrated nitric acid, and cover the basin with a clock-glass. Heat gently until the alloy is completely disintegrated. Remove and rinse the cover-glass, and evaporate to dryness on the steam-bath. Add 5 c.c. of dilute nitric acid and 20 c.c. of water, and heat until boiling. Filter. Wash the stannic oxide with hot water containing a little nitric acid, and then thoroughly with water alone.

Dry the stannic oxide in the steam-oven. Incinerate the filter paper, together with the stannic oxide, in a porcelain crucible at as low a temperature as possible. When all the carbon has been burnt off, allow the crucible to cool, and add several drops of concentrated nitric acid to oxidise any reduced oxide. Heat gently until dry, and then ignite with a Méker burner until of constant weight. In order to exclude flame gases during the ignition, it is advisable to support the crucible on a silica plate (p. 144).

The stannic oxide may contain antimony oxide. It always contains some lead oxide, but if the procedure has been carefully followed, the amount of occluded lead oxide will not usually exceed one milligram.

Determine the lead (in the filtrate from the stannic oxide) as sulphate or as chromate (p. 230). If the chromate method is used, add about 10 grams of sodium acetate in order to replace the nitric acid by acetic acid.

OUTLINE OF SECOND METHOD.—One portion of the alloy is dissolved in hydrochloric acid and the solution is evaporated to dryness. The residue is extracted with alcohol and the *lead chloride*, which is insoluble in alcohol, is weighed. Another portion of the alloy is dissolved in hydrochloric acid (with careful exclusion of air) and the *tin* in solution is determined volumetrically by means

of standard iodine. In a third portion the *antimony* is determined volumetrically by standard potassium permanganate or potassium bromate.

Determination of Lead.—In a small conical flask warm about 0.5 gram of the alloy on the steam-bath with 20 c.c. of concentrated hydrochloric acid. If it dissolves very slowly, pass chlorine gas¹ through the hot liquid until solution is complete. Transfer the solution to a basin and evaporate on the steam-bath almost to dryness. Add 20 c.c. of absolute alcohol and stir well. Filter through a Gooch crucible, and wash the lead chloride with absolute alcohol. In presence of antimony, it is better to use absolute alcohol containing about 1 per cent. of hydrochloric acid (gas). Dry the PbCl_2 in the steam-oven, and weigh.

Determination of Tin.—Fit a 200 c.c. flask with a rubber stopper and delivery tube as shown in Fig. 33, p. 93. Place 25 c.c. of concentrated hydrochloric acid in the flask, together with about 1 gram of marble in order to displace the air by carbon dioxide. Introduce about 0.2 gram (accurately weighed) of the solder, and at once insert the stopper and delivery tube. Warm the acid gently (but do not boil)—the delivery tube meantime dipping into water contained in a small beaker. (Care must be taken, by maintaining a steady flame, to prevent the water running back into the flask.) When the solder has completely dissolved, remove the beaker of water and substitute another beaker containing sodium carbonate solution. Allow the solution to cool. Cooling may be hastened by holding the flask under the tap—the delivery tube remaining in the sodium carbonate solution during the process.

When the solution is cold, drop a small chip of marble into it, and add about 75 c.c. of cold air-free water (water that has been recently boiled and rapidly cooled). Titrate the solution at once with decinormal iodine, using starch as indicator.

The iodine solution must be standardised by means of pure tin (0.15 gram), or with standard sodium arsenite (p. 107).

¹ The chlorine may be readily obtained by very gently warming a small quantity of potassium permanganate with concentrated hydrochloric acid in a small flask.

Determination of Antimony.—Disintegrate about 1 gram of the alloy by heating with 20 c.c. of concentrated sulphuric acid as described on p. 89, and determine the antimony volumetrically with either standard potassium permanganate (p. 89) or standard potassium bromate (p. 139).

ANALYSIS OF BRASS.

(Alloy of Copper and Zinc, with small quantities of Tin, Lead, and Iron.)

OUTLINE OF METHOD.—In one portion of the alloy, dissolved in nitric acid, the *copper* is determined either volumetrically, electrolytically, or gravimetrically as cuprous thiocyanate. After removal of copper, the *iron* is determined volumetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another (large) portion of the alloy is disintegrated with nitric acid. The *tin* is oxidised to stannic oxide which is weighed, and the *lead* in solution is determined as lead sulphate.

Determination of Copper.

(1) **Volumetric Method.**—In a conical flask dissolve about 1 gram of the alloy by gently warming with a mixture of 5 c.c. of concentrated nitric acid and 5 c.c. of water. Dilute the solution with 20 c.c. of water and boil briskly for two minutes. Add about 0.5 gram of urea to destroy nitrous acid. Add ammonia until a precipitate forms, and redissolve the precipitate in acetic acid. Cool, and dilute to 100 c.c. in a standard flask. Determine the copper in 25 c.c. volumetrically (p. 109).

(2) **Electrolytic Method.**—Dissolve 0.5 gram of the alloy in a mixture of 8 c.c. of concentrated nitric acid and 8 c.c. of water in a 200 c.c. beaker, and boil the solution gently for two minutes. Add 5 c.c. of dilute sulphuric acid, dilute to 150 c.c., and electrolyse with a rotating cathode (p. 183). If stationary electrodes are to be used, proceed as follows:—In a porcelain basin dissolve 0.5 gram of the alloy by warming with a mixture of 3 c.c. of concentrated nitric acid and 3 c.c. of water. Evaporate almost to dryness on the steam-bath. Add 5 c.c. of concentrated sulphuric acid and heat cautiously on a sand-bath until all nitric acid is expelled and copious fumes of sulphuric acid appear.

Allow to cool, add 20 c.c. of water cautiously, and stir to dissolve copper and zinc sulphates. Transfer the solution to a weighed platinum basin, dilute to 100 c.c., and electrolyse for about twelve hours (overnight), using a single accumulator (p. 182). Then rinse the cover-glass into the basin, and increase the current to 0.5 ampere (using two cells and the necessary resistance) for about an hour. When the deposition is complete, switch off the current, pour the solution at once into a beaker, and rinse the electrodes exactly as described on p. 182. Dry and weigh the cathode. (Keep the solution for the determination of iron and zinc.)

(3) **Gravimetric Method.**—In a covered porcelain basin dissolve 0.2 to 0.25 gram of the alloy by warming with a mixture of 2 c.c. of concentrated nitric acid and 2 c.c. of water. If any stannic oxide remains, dilute with a little water, filter through a small paper, wash with hot water, and receive the filtrate in a porcelain basin. Add 1 c.c. of concentrated sulphuric acid and evaporate until all nitric acid is expelled. Cool, add 25 c.c. of water, and filter to remove any lead sulphate; wash with dilute (normal) sulphuric acid. (Reject any stannic oxide and lead sulphate, the amounts of which in 0.25 gram are usually exceedingly small.) Add ammonia to the filtrate until it is only slightly acid. Determine the copper as cuprous thiocyanate (p. 225). (The filtrate may be used for the determination of iron and zinc.)

Determination of Iron and Zinc.

(1) **After Separation of Copper by Electrolysis.**—Evaporate the solution to about 30 c.c. If any stannic oxide separates, filter through a small paper, and wash thoroughly. Receive the filtrate in a 250 c.c. beaker. Add 2 c.c. of concentrated nitric acid, heat until boiling, and then add ammonia until alkaline. Boil for a moment, filter through a small paper, and wash twice with hot water. Set the filtrate aside. Dissolve the precipitate by pouring 10 c.c. of hot, dilute nitric acid into the filter, and receive the solution in the original beaker. Wash the filter paper. Reprecipitate the iron with ammonia. Filter through the same paper and wash thoroughly. Dissolve the precipitate

in 10 c.c. of hot, dilute hydrochloric acid, wash the filter paper, and titrate the solution with standard titanous chloride (p. 136); or dilute the solution to 100 c.c. in a standard flask and determine the iron colorimetrically (p. 192).

Mix the two filtrates from the iron precipitation, evaporate to about 100 c.c., and determine the zinc as zinc ammonium phosphate (p. 263).

(2) **After Separation of Copper as Cuprous Thiocyanate.**—Evaporate the filtrate to about 30 c.c. To the hot solution add concentrated nitric acid, drop by drop, until the decomposition of the thiocyanate is complete. Determine the iron and zinc as already described.

Determination of Tin and Lead.

Place 5 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 15 c.c. of concentrated nitric acid and 15 c.c. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is pasty. Add 5 c.c. of concentrated nitric acid, stir, and warm gently for several minutes. Then add 50 c.c. of water and heat until almost boiling. Filter through a small paper, wash with hot water containing a little nitric acid, and then with water alone. Dry, ignite, and weigh the stannic oxide (p. 272).

Transfer the filtrate to a porcelain basin, and add 8 c.c. of concentrated sulphuric acid. Evaporate on the steam-bath as far as possible, and then on a sand-bath until copious fumes of sulphuric acid are evolved. Cool, add 100 c.c. of water cautiously, and stir to dissolve the copper and zinc sulphates. Set aside for an hour. Filter through a Gooch crucible, wash with dilute (1 : 30) sulphuric acid and then with alcohol. Dry, and weigh the lead sulphate (p. 231).

ANALYSIS OF A BRONZE.

A bronze is an alloy consisting essentially of copper and tin, but usually containing also some zinc, together with traces of lead, nickel, and iron. Gun metal is composed nominally of ninety parts of copper and ten parts of tin. English bronze coins contain about ninety-five parts of copper,

four parts of tin, and one part of zinc. The amount of lead in bronze coins rarely exceeds 0.1 per cent., but much larger proportions of lead are present in some varieties of bronze. Aluminium bronze usually consists of about ninety parts of copper and ten parts of aluminium, but may contain tin and other metals.

It is assumed that the alloy under analysis contains copper, tin, and zinc, with traces of iron and lead. The method described will therefore apply to most varieties of bronze, slight modifications being necessary when aluminium or nickel is present.

OUTLINE OF METHOD.—One portion of the alloy is disintegrated with nitric acid. The insoluble stannic acid is filtered and washed, dissolved in a mixture of concentrated sulphuric and hydrochloric acids, and the *tin* in solution determined volumetrically. In the filtrate from the stannic acid, the *lead* is determined as lead sulphate. Copper is then removed by electrolysis, and the *iron* is determined volumetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another portion of the alloy is dissolved in aqua regia and the *copper* in solution is determined volumetrically.

Determination of Tin.—Place 2 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 10 c.c. of concentrated nitric acid and 10 c.c. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is pasty. Add 5 c.c. of concentrated nitric acid and warm gently for several minutes. Then add 30 c.c. of water and heat until almost boiling. Filter through an untared Gooch crucible, and wash the stannic acid with warm water containing nitric acid and then with water alone.

Transfer the stannic acid and the asbestos to a 400 c.c. conical flask, using about 25 c.c. of water. Add (cautiously) an equal volume of concentrated sulphuric acid, and boil for two minutes. Take care to avoid “bumping.” Then add 50 c.c. of concentrated hydrochloric acid and boil for two minutes. (The stannic acid dissolves, although the presence of the asbestos obscures this.) Reduce the stannic salt with antimony powder and determine the tin by titration with decinormal iodine (p. 118).

Determination of Lead.—In the filtrate from the stannic acid, determine the lead as lead sulphate. The procedure is given under brass (p. 276).

Removal of Copper.—Electrolyse the solution (after the removal of tin and lead), using either stationary electrodes (p. 181) or a rotating cathode (p. 183). The weight of copper deposited may serve for a determination of the copper, but the result will be slightly low as part of the copper is retained by the stannic acid.

Determination of Iron and Zinc.—Evaporate the solution (after removal of tin, lead, and copper) to about 20 c.c., and determine the iron and zinc as described under brass (p. 275).

Determination of Copper.—Dissolve 0.6 gram of the alloy by warming with a mixture of 6 c.c. of concentrated hydrochloric acid and 2 c.c. of concentrated nitric acid in a 200 c.c. flask. Boil the solution gently to expel excess of acid. Dilute with a little water, add ammonia until a precipitate forms, and then acidify with acetic acid. (The stannic acid precipitated by the ammonia does not wholly redissolve in the acetic acid.) Cool the solution and dilute to 100 c.c. in a standard flask. Determine the copper in 25 c.c. volumetrically (p. 109).

ANALYSIS OF A FUSIBLE ALLOY.

(Alloy of Bismuth, Lead, Tin, and Cadmium.)

The best known fusible alloys are Newton's alloy (two parts of bismuth, five parts of lead, and three parts of tin), Rose's alloy (two parts of bismuth, one part of lead, and one part of tin), and Wood's alloy (four parts of bismuth, two parts of lead, one part of tin, and one part of cadmium). The method described below is applicable to any of these alloys.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid.

The insoluble residue of impure stannic oxide is washed, dried, ignited, and weighed; it is then fused with sodium carbonate and sulphur. The soluble sodium thiostannate is removed by extraction with water. The insoluble residue of lead and bismuth sulphides is dissolved in dilute nitric acid. The bismuth is determined as basic

nitrate, the lead as sulphate, and the necessary corrections for the amounts thus found applied to the tin, lead, and bismuth.

The filtrate contains bismuth, lead, and cadmium, as nitrates. After separation of the bismuth as oxynitrate, the lead is determined as sulphate. The cadmium is determined either electrolytically or by precipitation as sulphide.

Place a weighed portion (about 0.6 gram) of the finely divided alloy in a covered porcelain basin, add 10 c.c. of concentrated nitric acid, and proceed as in the case of solder (p. 272), the acid being kept as concentrated as possible. When the reaction is complete, add about 30 c.c. of water, and boil gently for a few minutes. Filter, and wash the insoluble residue, at first with hot, dilute nitric acid, and then thoroughly with hot water.

Analysis of the Insoluble Residue.

Determination of Tin.—The insoluble residue consists of stannic oxide, with traces of bismuth and lead oxides. Dry, ignite, and weigh the impure stannic oxide as described on p. 272. After weighing the oxide, transfer it to a small mortar, powder it, and mix it with six times its weight of equal parts of pure sulphur and anhydrous sodium carbonate. Heat the mixture in a *covered* crucible, gently at first and then with a full Bunsen flame for five minutes. Allow the crucible to cool before removing the lid. Place the crucible in a beaker and boil with 100 c.c. of water. The tin dissolves as sodium thiostannate and the lead and bismuth remain as insoluble sulphides. Filter, wash the residue, incinerate the filter, and repeat the fusion. (As a rule, a single fusion is insufficient to bring all the stannic oxide into solution.) Extract with water, filter through a Gooch crucible, and wash the insoluble residue of lead and bismuth sulphides. Then pour boiling dilute nitric acid through the filter until the residue has dissolved. (A trace of the lead sulphide may be converted into insoluble lead sulphate; in case this has happened, use the same crucible for the filtration of the lead sulphate at a later stage.) Evaporate almost to dryness, dilute to about 20 c.c., and add *very dilute* ammonia until the solution is only slightly acid. Filter, wash the basic bismuth nitrate with dilute ammonium nitrate solution, and

convert it into oxide as described on p. 212. Weigh the Bi_2O_3 . To the filtrate from the basic bismuth nitrate, add 1 c.c. of concentrated sulphuric acid and evaporate until dense white fumes are evolved. Proceed with the determination of the lead as described on p. 231. Weigh the PbSO_4 .

Calculate the weight of PbO corresponding to the weight of PbSO_4 obtained. Subtract the weights of lead and bismuth oxides from that of the impure stannic oxide, in order to obtain the weight of pure stannic oxide.

Analysis of the Soluble Portion.

Determination of Bismuth.—The bismuth may be separated as basic nitrate, as described on p. 211. The following modification of the procedure is preferable, as it avoids the large dilution.

Evaporate the filtrate and washings on the steam-bath until the solution attains a syrupy consistency. Add 20 c.c. of water, stir thoroughly, and again evaporate. Add about 100 c.c. of dilute (2 grams per litre) ammonium nitrate solution, and keep the mixture for an hour, with occasional vigorous stirring, before filtering. Wash the bismuth oxynitrate with dilute ammonium nitrate solution. Convert the bismuth oxynitrate into oxide, as described on p. 212, and weigh as Bi_2O_3 . Add the weight of bismuth oxide found in the crude stannic oxide.

Determination of Lead.—To the filtrate from the bismuth oxynitrate, add 5 c.c. of concentrated sulphuric acid, and evaporate until dense white fumes of sulphuric acid are evolved. Proceed as directed on p. 231, but wash carefully about eight times with dilute (about normal) sulphuric acid before washing with alcohol; reject the alcohol washings. Weigh the PbSO_4 , and add the amount found in the analysis of the insoluble residue.

Determination of Cadmium.—Determine the cadmium in the filtrate either electrolytically, as described on p. 186, or by precipitation as sulphide and conversion into sulphate. (For details, see p. 214.)

ANALYSIS OF A LIMESTONE OR DOLOMITE.

Limestone consists essentially of calcium carbonate, but may contain also some magnesium carbonate. If the proportion of magnesium carbonate is considerable, the rock is called a dolomite. The usual minor constituents are iron, aluminium, silica (either free or combined), and sometimes traces of carbonaceous matter, phosphate, and manganese. A careful qualitative analysis must therefore precede the quantitative analysis.

In the following description of the analysis, it is assumed that a dolomite containing magnesium and calcium carbonates with small quantities of iron, aluminium, silica (or silicate), and phosphate is under examination. The results of the analysis of a rock are usually stated in terms of the constituent basic and acidic oxides, expressed as percentages. In dolomite, for example, the results are given in terms of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , CO_2 , P_2O_5 , and H_2O , and it is convenient to tabulate them in that order.

OUTLINE OF METHOD.—The silica and silicates are separated from the remainder of the rock by treatment with hydrochloric acid. The soluble and insoluble portions are examined separately.

In the soluble portion (1) *iron* and *aluminium*, together with any phosphate, are precipitated by ammonia; (2) in the filtrate, *calcium* is determined by precipitation as oxalate; (3) after removal of the calcium, *magnesium* is determined as phosphate.

The insoluble residue, after ignition, may be reported simply as *silica and insoluble silicates*; or, after fusion with sodium carbonate, the silica may be separated, and a complete analysis made.

In separate portions of the original mineral, *carbonate*, *water*, and *phosphate* are determined.

Separation into Soluble and Insoluble Portions.

Reduce about 10 grams of dolomite to a fine powder, and place the powder at once in a stoppered weighing-bottle. Take portions of this powder as required, the weight of each portion being found by difference.

Place a weighed portion (about 1.5 gram) in a porcelain basin, and cover the basin with a clock-glass to prevent loss during effervescence. Moisten the powder with a little water,

and, by means of a pipette, introduce through the spout of the basin 10 c.c. of concentrated hydrochloric acid. When the action has almost ceased, rinse the cover-glass and the side of the basin with water, and boil for a few minutes. Again rinse the cover-glass and remove it. Evaporate to dryness—as far as possible on the steam-bath, and afterwards on a *gently heated* sand-bath.

Add 5 c.c. of concentrated hydrochloric acid to the dry mass, and after about a minute dilute with about 10 c.c. of water; warm the covered basin on the steam-bath. Filter through a 7-cm. or 9-cm. paper and receive the filtrate in a 250 c.c. beaker. Add a few drops of dilute hydrochloric acid to the basin and carefully rinse the insoluble residue into the filter with a *fine* jet of hot water. Remove any traces of silica adhering to the basin or stirring-rod with a small piece of filter paper and drop this into the filter. Rinse the basin into the filter once more, and then wash the insoluble residue about ten times with small (2 c.c.) portions of hot water. A few drops of the last washing should give no turbidity with silver nitrate. The insoluble residue consists of silica and insoluble silicates; the filtrate, which should not much exceed 50 c.c. in volume, contains the main portion of the metallic radicals as chloride.

Analysis of the Soluble Portion.

For the most exact work, the trace of silica present in the solution must be removed by a second evaporation to dryness (*cf.* p. 255), but for all ordinary purposes this is unnecessary.

Determination of Iron and Aluminium.—Add 3 c.c. of concentrated nitric acid in order to oxidise any ferrous salt and to form ammonium nitrate when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 5 c.c. of concentrated ammonia diluted with 5 c.c. of water. Then add dilute ammonia, drop by drop, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. Boil for one minute. Filter, and wash three times with hot water, without necessarily bringing every trace of the precipitate on to the filter paper. Set the

filtrate aside. The precipitate is mainly ferric and aluminium hydroxides (together with any phosphate), but contains also traces of calcium and magnesium salts which must be removed by reprecipitation. Dissolve the precipitate by pouring about 10 c.c. of hot, dilute nitric acid over the filter paper and receive the solution in the original beaker. Wash the paper a few times with hot water, and preserve it until required later. To the filtrate, add about 2 c.c. of concentrated nitric acid, and precipitate the iron and aluminium as before. Filter through the same filter paper, combining the filtrate with that from the first precipitation, and wash thoroughly with hot water. Incinerate the filter paper together with the precipitate without preliminary drying. Ignite the oxides in the open, slightly inclined crucible (to allow access of air) with a Méker burner. Cool, and weigh the Fe_2O_3 and Al_2O_3 .

The iron and aluminium in the mixed oxides are determined as follows:—Add to the crucible containing the ignited precipitate about 2 grams of potassium pyrosulphate. Heat gently over a small flame, and proceed with the fusion as described in detail on p. 287. When no more undissolved particles are visible, allow the crucible to cool, add 2 c.c. of concentrated sulphuric acid, and melt the contents of the crucible again. After cooling, place the crucible in a beaker with 50 c.c. of water and heat until solution is complete, except for a trace of silica. Remove the crucible and rinse it. Without filtering, and after cooling, add 20 c.c. of 20 per cent. ammonium thiocyanate solution, and titrate with standard titanous chloride (p. 136). Calculate the weight of ferric oxide in the mixed oxides. The difference between the weight of the mixed oxides and the weight of the ferric oxide gives the weight of the alumina.

If phosphate is present, it should be determined in a separate portion of the mineral (p. 285), and a correction applied to the alumina. Calculate the phosphate as P_2O_5 , and subtract this from the weight of alumina as determined above.

Determination of Calcium.—To the combined filtrates add 1 c.c. of methyl orange and sufficient hydrochloric acid to make the solution faintly acid. Evaporate to about 200 c.c.

Heat the solution to the boiling-point in a 400 c.c. beaker. Remove the flame and add about 3 grams of solid ammonium oxalate. Make the solution distinctly alkaline with ammonia, and boil gently until the precipitate becomes granular. Keep the mixture for one hour, decant the supernatant liquid through a filter, and wash three or four times with hot water, retaining the precipitate, as far as possible, in the beaker. Dissolve the impure calcium oxalate in hot, dilute nitric acid (5 c.c. of concentrated acid mixed with 10 c.c. of water), dilute the solution to about 200 c.c., heat until boiling, and reprecipitate the calcium oxalate by adding about 2 c.c. of ammonium oxalate solution and then ammonia, drop by drop, until the liquid is alkaline. Boil for a few minutes and set the beaker aside for an hour. (If magnesium is present only in traces, one precipitation is sufficient.) Proceed according to the directions on p. 177. Combine the filtrates from the two precipitations.

Determination of Magnesium.—Acidify the combined filtrates and evaporate to about 300 c.c. Add about 2 c.c. of methyl orange, and then ammonia until the solution is neutral. Heat until boiling, and add a decided excess of microcosmic salt (2.5 grams for dolomite; 1 gram for limestone) to the boiling solution. Cool, add 5 c.c. of concentrated ammonia, and set the solution aside for at least twelve hours (preferably twenty-four hours). Filter, and wash with dilute ammonia. Dissolve the precipitate in the minimum amount of dilute hydrochloric acid, and wash the filter paper. Reprecipitate the magnesium ammonium phosphate by adding *a few drops* of microcosmic salt solution and then ammonia until the liquid is decidedly ammoniacal. Stir the mixture briskly, and set the beaker aside for a few hours. Then proceed according to the directions on p. 173.

Analysis of the Insoluble Portion.

Incinerate the filter, without preliminary drying, and ignite the insoluble residue in a platinum crucible, and weigh. If the insoluble portion amounts to less than 2 per cent., it is sufficient for most purposes to report the amount of "silica and insoluble silicates"; if it exceeds that amount, analyse it according to the following scheme.

Determination of Silica.—Ignite the insoluble residue with the filter paper in a platinum crucible. To the residue add about six times its weight of anhydrous sodium carbonate, and proceed according to the directions given on p. 253 for the determination of silica in an insoluble silicate.

The filtrate from the silica may contain any of the constituents found in the soluble portion. It may be added to the main solution, or it may be analysed apart from, and in the same manner as, the main solution.

Determination of Other Constituents.

Separate portions of the original mineral must be used for the determination of water, carbonate, and phosphate.

Water.—Determine the amount of water by Penfield's method, using about 2 grams of the mineral for the determination. For details, see p. 261.

Carbonate.—Determine the carbonate by the direct method (p. 215). Use about 1 gram of the dolomite for the determination.

Phosphate.—The amount present is often so small as to be negligible. If it is to be determined, 2 to 5 grams of the dolomite should be decomposed with dilute nitric acid. After evaporation to dryness and removal of silica, the phosphate is determined in the soluble portion by the molybdate method (p. 242).

ANALYSIS OF AN INSOLUBLE SILICATE.

(Feldspar, Clay, Mica, etc.)

Most of the natural silicates, such as clay, feldspar, garnet, and mica, are complex alumino-silicates. For example, orthoclase (potassium feldspar) may be represented as KAlSi_3O_8 ; anorthite (calcium feldspar) as $\text{CaAl}_2\text{Si}_2\text{O}_8$; albite as $\text{NaAlSi}_3\text{O}_8$; kaolinite as $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$; and muscovite (common or potassium mica) as $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$. Pure forms of these minerals are, however, almost unknown; thus, although orthoclase has essentially the composition

represented by KAlSi_3O_8 , in almost all specimens it is found that the potassium is to some extent replaced by sodium, calcium, and magnesium, whilst the aluminium is usually partially replaced by iron. Titanium is almost invariably present. The analysis of a silicate therefore involves, as a rule, the determination of silica, aluminium, iron, titanium, calcium, magnesium, sodium, potassium, and, in some cases, phosphate, carbonate, and water.

Full information on this important branch of analytical chemistry, with details for the analysis of more complex silicates, will be found in Hillebrand's *Analysis of Silicate and Carbonate Rocks*; the practical details of manipulation are minutely described in Washington's *Chemical Analysis of Rocks*.

OUTLINE OF METHOD.—A portion of the silicate is fused with sodium carbonate, and the fused mass is extracted with excess of acid. The insoluble residue is *silica*. The filtrate contains the iron, aluminium, titanium, calcium, and magnesium, which are determined as follows: *Iron*, *aluminium*, and *titanium* are precipitated by ammonia, the amount of iron in the mixed precipitate being determined volumetrically and the titanium colorimetrically. After removal of the iron, aluminium, and titanium, *calcium* is precipitated as oxalate. After removal of the calcium, *magnesium* is determined as phosphate.

Separate portions of the silicate are used for the determination of (1) *sodium* and *potassium* by the Lawrence Smith method; (2) *water*; (3) *carbonate*; and (4) *phosphate*.

Break the mineral into small pieces on a clean steel plate. Take about 10 grams of clean pieces of the mineral, and crush in a percussion mortar to a coarse powder. Then grind to a fine powder in an agate mortar. The whole analysis is facilitated by reducing the mineral to a fine powder, but only for the determination of the alkalis is it essential to grind to the finest possible powder. The various constituents of a rock often differ very much in hardness, and it is not permissible to reject the portion that offers most resistance to grinding, since this portion probably differs in composition from the remainder. When, therefore, *the whole* of the sample has been reduced to a fine powder, mix it thoroughly, place in a stoppered bottle, and use portions of this powder for each of the following analyses.

Determination of Silica, Iron, Aluminium, Titanium, Calcium, and Magnesium.

Fusion with Sodium Carbonate.—Take a weighed portion (0.9 to 1.1 gram) of the powder, and fuse it with 6 grams of anhydrous sodium carbonate. (For details of the procedure, see p. 253.)

Determination of Silica.—Details for the separation of the silica after the fusion are given on pp. 253-256.

Determination of Iron, Aluminium, and Titanium.—Add to the filtrate from the silica about 5 c.c. of concentrated hydrochloric acid—in order to provide sufficient ammonium chloride to prevent precipitation of magnesium when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 7 c.c. of concentrated ammonia diluted with 7 c.c. of water. Then add dilute ammonia, drop by drop, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. Boil for one minute. Following the procedure described under dolomite (p. 282), filter and wash the precipitate (use an 11-cm. paper if necessary), dissolve in nitric acid, and reprecipitate with ammonia as before. Add a *small* quantity of well-washed paper pulp (see p. 30), and boil for about a minute. (The paper pulp facilitates the washing of the precipitate, its reoxidation during ignition, and especially its subsequent solution in fused pyrosulphate.) Filter and wash the precipitate. Ignite and weigh the mixture of Fe_2O_3 , Al_2O_3 , and TiO_2 in the platinum crucible containing the non-volatile residue from the silica (see p. 256).

Add to the crucible containing the ignited precipitate about 10 grams of coarsely powdered potassium hydrogen sulphate (previously fused until spluttering ceases to convert it into pyrosulphate). Heat gently over a small flame until the salt is fused, and after any moisture has been driven off (about thirty minutes) gradually increase the temperature—care being taken to avoid boiling or spluttering—until white vapour of sulphur trioxide is slowly given off. Continue heating until the particles of precipitate have entirely disappeared, the temperature being gradually raised until, towards the end of the operation, the bottom of the

crucible is at very faint redness. By removing the flame and allowing the crucible to cool somewhat, the fused mass becomes less opaque and it is possible to see in a good light whether all the precipitate has dissolved. When no more undissolved precipitate is visible, heat for a few minutes longer and then allow the crucible to cool.

Add 5 c.c. of concentrated sulphuric acid and melt the contents of the crucible again. Cool, place the crucible with about 100 c.c. of water in a beaker, and heat gently. When the crucible is free from adhering sulphate, remove and rinse it. If the fusion has been successful, only traces of silica remain undissolved. Filter through a small paper and wash the silica. Ignite and weigh the silica in a platinum crucible, correct it for impurity (p. 255), and add the amount to the weight of the main silica precipitate. After volatilising the silica, fuse the slight residue in the crucible with a small piece of pyrosulphate, and add this to the main solution for the determination of iron, aluminium, and titanium.

Determination of the Iron.—Dilute the filtrate to about 200 c.c., reduce the iron to the ferrous state by means of hydrogen sulphide, and determine the iron volumetrically (p. 97). If titanium is not to be determined, the solution may be titrated with standard titanous chloride—without previous reduction of the iron (p. 136).

Determination of the Titanium.—Evaporate the titrated solution to about 150 c.c. and transfer it to a 250 c.c. graduated flask. Add 10 c.c. of hydrogen peroxide and dilute to the graduation mark. Determine the titanium colorimetrically (p. 194).

Determination of the Aluminium.—From the total weight of the ammonia precipitate deduct the weights of Fe_2O_3 , TiO_2 , and SiO_2 obtained as above. The weight of Al_2O_3 is thus found. (If phosphate is present, it is determined in a separate portion of the mineral (p. 291) and the corresponding weight of P_2O_5 is deducted from the weight of alumina.)

Determination of Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 283).

Determination of Sodium and Potassium.

(*Lawrence Smith Method.*)

OUTLINE OF METHOD.—The silicate is decomposed by heating with ammonium chloride and calcium carbonate. The mass is extracted with water, and a solution of the chlorides of calcium, sodium, and potassium is obtained. The calcium is removed, partly as carbonate and the remainder as oxalate. The sodium and potassium are then determined in the usual manner.

The ammonium chloride must be pure, and it is advisable to sublime a sample for the special purpose of this determination. The calcium carbonate must be specially purified. The purest obtainable calcium carbonate (or pure calcspar) is dissolved in hydrochloric acid contained in a porcelain basin. Excess of ammonia is added to the solution which is heated almost to the boiling-point, and a freshly prepared solution of pure ammonium carbonate is then added. The precipitate is collected in a Büchner funnel, washed *very thoroughly* with hot water, and dried. Even after this purification, it may still contain traces of alkalis, derived probably from the vessels employed. A blank experiment must therefore be carried out with the same quantities of the reagents and in the same manner as in the actual analysis, and the necessary correction applied in subsequent analyses. If the weight of alkali chloride from 0.5 gram of ammonium chloride and 4 grams of calcium carbonate exceeds 2 mgrms., further purification of the reagents is necessary.

For a successful determination of the alkalis, it is in most cases essential that the substance should be ground to the finest possible powder. When mica is present, it cannot be reduced to a very fine powder on account of its ready cleavage into plates and the flexibility of these plates; mica, however, is more readily decomposed than most silicates, and less thorough grinding suffices for it.

A special finger-shaped platinum crucible is most suitable for the ignition, but an ordinary 30 c.c. crucible is quite satisfactory. Certain precautions are necessary to prevent loss of the alkali chlorides by volatilisation. The crucible, with a well-fitting lid, should be supported on a perforated asbestos board or silica plate (p. 144) so that the lowest third, but not more, can be heated to a red heat.

Decomposition of the Silicate.—Weigh, by difference, about 0.5 gram of the silicate into a platinum basin (or a large agate mortar). Add 0.5 gram of ammonium chloride and mix the powders very thoroughly by gentle rubbing and stirring with a small agate pestle. Weigh approximately 4 grams of calcium carbonate, add most of this to the basin, and continue the stirring and rubbing until thorough mixing has resulted. Place the platinum crucible on a sheet of glazed paper and put into it sufficient calcium carbonate to cover the bottom (in order to prevent adhesion of the mass after the ignition). With the aid of a small spatula, transfer the mixture very carefully from the basin to the crucible. Rinse the basin and clean the spatula with the remainder of the calcium carbonate and add this (together with any powder that has fallen on the glazed paper) to the crucible.

Support the covered crucible in a hole of appropriate size cut in asbestos board, and heat with a small flame for about ten minutes. When the odour of ammonia is no longer perceptible, increase the flame until the lower part of the crucible is heated somewhat above dull redness, and continue the heating for about forty minutes.

Allow the crucible to cool. Add 3 to 4 c.c. of water to slake the quicklime that has been formed and to disintegrate the mass. After a few minutes transfer the contents of the crucible to a porcelain basin, detach any adhering portions with a platinum spatula (or a glass rod), and rinse the crucible with about 50 c.c. of hot water. (Use a wash-bottle of resistant glass.) Carefully break down any lumps with an agate pestle, and boil gently for a few minutes. Filter into a beaker (of resistant glass) and wash the residue thoroughly with about 150 c.c. of hot water. The solution contains all the alkali chloride, together with some calcium chloride.

Removal of Calcium.—To the hot solution add 10 c.c. of ammonia, and about 2 grams of ammonium carbonate dissolved in cold water. Filter into a 6-inch porcelain basin, and wash the calcium carbonate thoroughly with hot water. Evaporate the filtrate to about 50 c.c., transfer it to a platinum basin, and evaporate to complete dryness on the steam-bath. Heat the covered basin in an air-oven at 140° for an hour, and then expel ammonium salts by gentle ignition (see p. 251).

The residue still contains a trace of calcium and possibly sulphate which are removed as follows:—Dissolve the residue in 3 to 4 c.c. of water; add 1 drop of barium chloride, 1 c.c. of ammonium carbonate, and a few drops of ammonium oxalate. Evaporate almost to dryness on the steam-bath. Add 3 to 4 c.c. of water, filter through a small paper into a weighed platinum crucible, and wash the basin and the filter 6 to 8 times with warm water, using about 2 c.c. at a time. Add a drop of hydrochloric acid to the crucible, evaporate to dryness, and expel ammonium salts by gentle ignition. Finally heat the bottom of the crucible to very faint redness (barely visible in direct daylight), care being taken to avoid actual fusion of the alkali chlorides. Cool, and weigh.

Determination of Sodium and Potassium.—The weight of the residue gives the weight of the mixed sodium and potassium chlorides. Determine the potassium, either as perchlorate or as chloroplatinate, and find the amount of sodium by difference (p. 252)—after correcting for the impurity derived from the reagents, glass vessels, etc. It is usually assumed that the impurity contains no potassium chloride, and the correction disclosed by the blank determination falls, therefore, entirely on the sodium chloride.

Note.—If the mixed chlorides do not dissolve completely in water, collect the insoluble residue on a small filter paper, wash with hot water, ignite, and weigh. If the weight is less than 1 mgrm., subtract it from that of the mixed chlorides; if more than 1 mgrm., reject the analysis.

Determination of Water, Carbonate, and Phosphate.

Water and Carbonate.—Use separate portions of the powdered mineral for the determination of (1) water, as described on p. 261; and (2) carbonate, as described on p. 215. Many silicates contain no carbonate, but it is often found in clays.

Phosphate.—Weigh accurately about 1 gram of the powdered mineral into a small platinum basin. Add 10 c.c. of water and mix thoroughly by stirring with a platinum wire. Then add 10 c.c. of concentrated nitric acid and 5 c.c. of hydrofluoric acid. Evaporate to dryness on the steam-bath. Add 5 c.c. of nitric acid, evaporate again and repeat

the evaporation with nitric acid two or three times in order to decompose fluorides. Heat the dry residue until it becomes brown, add 15 c.c. of dilute nitric acid and boil gently for a few minutes in order to convert any meta- or pyrophosphate into orthophosphate. Filter, and wash with warm, dilute nitric acid. Determine the phosphate in the solution by the molybdate method (p. 242).

ANALYSIS OF A GLASS.

Ordinary "soft" glass, used for bottles, window glass, etc., is essentially a sodium-calcium silicate; in "hard" glass the sodium is replaced by potassium. Flint glass is a potassium-lead silicate. Pyrex glass contains about 12 per cent. of boric oxide, and Jena glass is a sodium-zinc borosilicate. Aluminium and traces of iron, manganese, and magnesium are present in most glasses. Oxides of cobalt, copper, iron, chromium, and manganese are used in the preparation of coloured glasses. Bone ash, cryolite, or fluorspar is added to common glass in order to render it opaque.

The commonest constituents of glass are therefore silica, sodium, potassium, calcium, lead, and aluminium, with traces of iron, manganese, and magnesium. The analysis of a glass is therefore carried out according to the procedure for an insoluble silicate, but when lead and manganese are present the method must be modified as follows:—

OUTLINE OF METHOD.—The glass is fused with sodium carbonate, and the fused mass is extracted with hydrochloric acid. *Silica* is determined in the insoluble residue. In the filtrate from the silica, the *lead* is precipitated as sulphide. After removal of lead, the *iron*, *aluminium*, and *manganese* are precipitated together by means of ammonia and ammonium persulphate and weighed as oxides; the iron in the mixed oxides is determined volumetrically. After removal of iron, aluminium, and manganese, *calcium* is precipitated as oxalate and *magnesium* as phosphate.

Separate portions of the glass are used for the determination of (1) *manganese* by the bismuthate method, (2) *sodium* and *potassium* by the Lawrence Smith method, (3) *hygroscopic water*.

Fusion with Sodium Carbonate and Determination of Silica.—Fuse a weighed portion (about 1 gram) of the finely powdered glass with sodium carbonate, as described

on p. 253. (If the glass contains lead, great care must be taken to maintain an oxidising atmosphere within the crucible, in order to avoid reduction of lead compounds and consequent serious damage to the crucible. The crucible must be placed on the triangle in a slightly inclined position so that the flame does not completely envelop it; and the sodium carbonate must be free from organic impurities, such as traces of paper and straw. A few centigrams of potassium nitrate may be mixed with the sodium carbonate in order to minimise the risk of reduction.) Wash the insoluble residue with hot, dilute hydrochloric acid and then *very thoroughly* with hot water, since the lead chloride is somewhat difficult to remove. Test the purity of the silica in the usual manner.

Determination of Lead.—To the filtrate from the silica (about 150 c.c.) contained in a 400 c.c. conical flask, add moderately concentrated ammonia until a faint turbidity is obtained. Then add 5 c.c. of concentrated hydrochloric acid. (In order to secure complete precipitation of the lead, the concentration of acid in the solution must not much exceed 0.3N.) Heat the solution to about 60° and saturate with hydrogen sulphide (Fig. 51, p. 174). Filter, and wash the precipitate with very dilute hydrochloric acid containing hydrogen sulphide. The precipitate, which may be light brown in colour on account of admixed sulphur, invariably contains a trace of platinum sulphide derived from the crucible in which the fusion was made.

Dissolve the lead sulphide by pouring 20 c.c. of boiling 5N hydrochloric acid into the filter in small portions, and receive the solution in a porcelain basin; wash the filter with hot water. Following the procedure described on p. 231, determine the lead in the solution as lead sulphate.

If only traces of lead are present, evaporate the lead chloride solution nearly to dryness, dilute to 100 c.c. in a standard flask, and determine the lead colorimetrically (p. 198).

Determination of Iron, Aluminium, and Manganese.

Evaporate the filtrate from the lead sulphide to 100 c.c. and transfer it to a 250 c.c. beaker. Add 3 c.c. of concentrated nitric acid (to oxidise ferrous salt and to provide sufficient

ammonium salt when ammonia is added) and heat until boiling. Remove the flame and neutralise most of the acid by adding 5 c.c. of concentrated ammonia diluted with 5 c.c. of water. Add 1 gram of ammonium persulphate, heat until boiling, and then add dilute ammonia until the solution is distinctly ammoniacal. Boil for not more than two minutes, and make sure that a faint ammoniacal odour persists.

Filter through a 9-cm. or 11-cm. paper (according to the amount of precipitate) and wash with a little hot water. Set the filtrate aside. Dissolve the precipitate in 10 to 20 c.c. of hot, 5N hydrochloric acid containing a few drops of sulphurous acid and receive the solution in the original beaker. Wash the filter paper. Reprecipitate with ammonia and ammonium persulphate, and add a small quantity of paper pulp (*cf.* p. 287). Filter, and wash thoroughly with hot water. Ignite the precipitate (with a Méker burner) in the platinum crucible containing the non-volatile residue from the silica (p. 256), and weigh the mixture of Fe_2O_3 , Al_2O_3 , Mn_3O_4 , and a trace of SiO_2 .

Determination of the Iron.—Fuse the precipitate with potassium pyrosulphate as described on p. 287. Separate and weigh the silica that is always found here (see p. 288), and determine the iron volumetrically. Calculate the percentage of Fe_2O_3 in the glass and also the weight of Fe_2O_3 in the ammonia precipitate.

Determination of the Manganese.—Place a weighed portion (about 1 gram) of the finely powdered glass in a platinum basin. Add 10 c.c. of sulphuric acid (1 : 1) and 5 c.c. of hydrofluoric acid, and mix thoroughly by stirring with a stout platinum wire. Warm the mixture gently, with frequent stirring, to decompose the powder, and then evaporate as far as possible on the steam-bath. Remove the basin to a sand-bath and heat more strongly until fumes of sulphuric acid are evolved. Cool, add 3 c.c. of concentrated sulphuric acid, dilute with a little water, and heat for a few minutes to dissolve soluble sulphates. Transfer the contents of the basin to a conical flask, dilute to 100 c.c., and heat until almost boiling. (As a rule the sulphates dissolve completely—except possibly lead sulphate.) Cool to 40° and determine the manganese in the solution by the bismuthate

method as described on p. 88 for manganese in iron ore. Calculate the percentage of MnO in the glass, and also the weight of Mn_3O_4 in the ammonia precipitate.

Determination of the Aluminium.—Deduct the weights of Fe_2O_3 , Mn_3O_4 , and SiO_2 (obtained as above) from the total weight of the ammonia precipitate. The weight of the Al_2O_3 in the precipitate is thus obtained and the percentage of Al_2O_3 in the glass may then be calculated.

Determination of Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 281).

Determination of Sodium and Potassium.—In a separate portion of the glass (about 0.5 gram) determine the sodium and potassium by the Lawrence Smith method (p. 289).

Determination of Water.—Glass powder is very hygroscopic, and it is advisable to determine the “hygroscopic water” by Penfield’s method (p. 261), and to express all results as percentages of the dry glass. Analyses of the same sample made at different times will then be comparable.

ANALYSIS OF IRON PYRITES.

Iron pyrites (pyrite) consists essentially of sulphide of iron, FeS_2 , and in a good specimen the amount of other elements is very small. In many specimens, however, the iron is partially replaced by copper, and traces of arsenic, cobalt, and nickel are often present. Most specimens contain also a certain amount of gangue—consisting of enclosed or adhering particles of sand or other siliceous matter.

The analysis of iron pyrites therefore involves, as a rule, the determination of “gangue,” copper, iron, and sulphur. It is sometimes necessary to determine also traces of arsenic, nickel, and cobalt, and the method described below must then be modified to include the determination of these elements.

Iron pyrites may be analysed by the method described on p. 298 for copper pyrites, but the following method is probably preferable.

OUTLINE OF METHOD.—The finely divided mineral is oxidised by means of sodium chlorate and hydrochloric acid. The *insoluble residue* is separated by filtration, ignited, and weighed. The *sulphur*, which has been completely oxidised to sulphate, is determined as follows:—The iron is precipitated by addition of ammonia, and, without filtering, the sulphate is precipitated as barium sulphate. The solution is then acidified with hydrochloric acid, in order to redissolve the ferric hydroxide, and the barium sulphate is collected and weighed.

The *copper* is precipitated from the filtrate as sulphide, and the *iron* is then determined either volumetrically or by precipitation as hydroxide.

Decomposition of the Pyrites.—Place about 0.3 gram of the *finely powdered* pyrites in a *dry*, 200 c.c. conical flask, mix with 2 grams of powdered sodium chlorate, moisten with 3 c.c. of water, and cool the flask and contents in ice. Add 20 c.c. of concentrated hydrochloric acid, previously cooled in ice, and keep the flask in the ice for twenty to thirty minutes, with occasional *gentle* shaking. Remove the flask from the ice, so that the temperature will rise slowly. After about thirty minutes, warm the flask momentarily on the steam-bath, repeating this at intervals with gentle shaking, until the pyrites has entirely disappeared. The decomposition should proceed without the separation of sulphur, the oxidation of which, if it is in the form of lumps or liquid globules, is exceedingly tedious.

Transfer the solution, together with any insoluble gangue, to a porcelain basin, and evaporate to dryness on the steam-bath. Cover the dry residue with 5 c.c. of concentrated hydrochloric acid, and, after five minutes, warm and add about 30 c.c. of water. Filter into a 400 c.c. beaker, and wash the residue with hot, dilute hydrochloric acid and then thoroughly with hot water. Incinerate the filter, ignite the residue strongly, and weigh. The residue consists, as a rule, of silica or insoluble silicates, and may usually be reported as “insoluble residue” or “gangue”; if, however, an analysis of it is required, proceed as directed on p. 256.

Determination of Sulphur.—Dilute the solution to about 200 c.c. with cold water, and add ammonia in excess to the cold solution to precipitate the iron. Heat the solution until boiling, and precipitate the sulphate with a boiling

solution of barium chloride, as described on p. 170. In order to estimate the quantity of reagent required, assume that the mineral is pure pyrites, and use 5 per cent. more than the calculated amount, dissolved in 25 c.c. of water.

Add dilute hydrochloric acid to the mixture in which the barium sulphate and ferric hydroxide are suspended, and, with frequent stirring, make sure that the latter has completely dissolved. (Avoid unnecessary excess of acid.) Cover the beaker and set it aside for at least six hours. The barium sulphate should appear perfectly white. Filter, wash, and weigh the barium sulphate.

Note.—The temporary removal of the iron from solution as ferric hydroxide is necessary in order to obtain the barium sulphate free from “occluded” ferric salts (see p. 170).

Determination of Copper.—In the filtrate from the barium sulphate determine the copper as sulphide, as described on p. 174.

Determination of Iron.—After removal of the copper, determine the iron either volumetrically (*a*) or by precipitation as hydroxide (*b*).

(*a*) Ascertain that the iron is present entirely as *ferrous* chloride; if not, saturate the solution again with hydrogen sulphide. Expel the hydrogen sulphide with a current of carbon dioxide at the boiling-point, and cool. Titrate the solution with standard potassium permanganate (see, however, p. 92) or potassium dichromate.

(*b*) Evaporate the solution in an open basin to expel hydrogen sulphide, and proceed as described on p. 159.

ANALYSIS OF COPPER PYRITES.

Copper pyrites (chalcopyrite) consists essentially of a copper-iron sulphide, CuFeS_2 , and in a good specimen of the mineral the amount of other elements is negligibly small. Many specimens contain traces of silver, and more or less gangue is usually present.

The analysis of copper pyrites therefore presents a problem very similar to that of iron pyrites. The same methods are applicable to both, and copper pyrites may be analysed

by the method described on p. 296, or, preferably, by the method described below.

OUTLINE OF METHOD.—In one portion of the mineral, the *sulphur* is oxidised by heating with sodium peroxide and sodium carbonate. The sulphate is then determined as barium sulphate.

Another portion of the mineral is decomposed with dilute nitric and sulphuric acids. The *insoluble residue* of silica, etc., is separated by filtration, ignited, and weighed. The *copper* in the solution is precipitated by means of aluminium and is collected on a Gooch filter, washed, dried, and weighed. The *iron* in the filtrate is determined volumetrically.

Determination of Sulphur.

In a spun-iron crucible of about 30 c.c. capacity mix 2 grams of dry sodium carbonate with 5 grams of sodium peroxide. Add a weighed quantity (about 0.3 gram) of the finely powdered pyrites and carefully mix the contents of the crucible by stirring gently with a nickel spatula or a glass rod. Place the crucible in a hole of appropriate size cut in asbestos board (Fig. 39, p. 144); heat very gently for about ten minutes, and then fuse the contents of the crucible by heating more strongly, but not above dull redness. Lift the asbestos board by opposite corners and rotate the crucible occasionally so as to rinse down the sides with the molten mixture.

Remove the flame and, as soon as the contents of the crucible become solid, place the crucible upright in a 500 c.c. beaker containing about 30 c.c. of water. Cover the beaker and upset the crucible with a glass rod. Warm gently to dissolve sodium salts, and then remove the crucible and rinse it into the beaker. Add (cautiously) 8 c.c. of concentrated hydrochloric acid to decompose some of the alkali hydroxide and carbonate. Filter through paper pulp (p. 30) and wash the precipitate thoroughly with hot water. Transfer the solution to a 500 c.c. beaker, neutralise (approximately) by adding concentrated hydrochloric acid, and then add 1 c.c. of acid in excess. Dilute the solution to about 250 c.c., heat until boiling, and precipitate the sulphate with a boiling solution of barium chloride in slight excess (p. 170). Set aside for at least six hours. Filter (a Gooch crucible may be used), wash, and ignite the barium sulphate.

Determination of Copper and Iron.

Place a weighed portion (about 0.4 gram) of the *finely powdered* pyrites in a porcelain basin or casserole provided with a cover-glass. Add 20 c.c. of water, 5 c.c. of concentrated nitric acid, and 5 c.c. of concentrated sulphuric acid. Warm very cautiously, adjusting the heating so that there is a vigorous, but not turbulent, evolution of brown fumes. If this operation is properly conducted, there will be no residue of sulphur after about ten minutes' treatment; if any sulphur remains, continue to boil gently with occasional addition of a few drops of concentrated nitric acid. (If the sulphur collects into a single large bead, it may be removed from the solution by means of a glass rod.)

When all the sulphur is oxidised, add a further 5 c.c. of concentrated sulphuric acid, and evaporate on a sand-bath until copious white fumes of sulphuric acid are evolved; cool, and dilute the solution to about 40 c.c. Heat the solution, and keep it hot until any anhydrous ferric sulphate has dissolved. Filter, wash with cold and then with hot water. Ignite and weigh the insoluble residue.

Determination of Copper.—Cut some sheet aluminium into pieces about 2 by 4 cm., and bend each piece at right angles across the middle. Place four of the pieces in the *hot* pyrites solution, cover the beaker, and heat gently on a hot-plate until the solution is colourless (about one hour). Cool the solution. Remove the aluminium with a glass rod and rinse the pieces carefully with a jet of water. Collect the precipitated copper in a Gooch crucible, wash thoroughly with cold water and three times with alcohol (reject the alcohol washings), and dry in a steam-oven for twenty minutes. Cool and weigh.

Determination of Iron.—Titrate the filtrate (without delay) with decinormal permanganate.

Note.—If the aluminium contains a trace of iron—which is very probable—a correction for this impurity is necessary, and the above procedure must be modified as follows:—(1) Weigh (to the nearest centigram) the aluminium sheet before and after using it to precipitate the copper. (2) In another beaker mix 80 c.c. of water and 10 c.c. of concentrated

sulphuric acid; add a weighed quantity of aluminium (four pieces), and warm on the hot-plate beside the pyrites solution. After cooling, remove the aluminium, dry and weigh it. Titrate the solution with decinormal permanganate. (3) From the data obtained in (1) and (2) calculate the correction to be applied to the titration of the iron.

ANALYSIS OF ZINC BLENDE.

Zinc blende consists essentially of zinc sulphide, but usually contains also traces of carbonate, cadmium, copper, lead, iron, and manganese. With most samples there is associated a certain amount of adhering siliceous matter.

OUTLINE OF METHOD.—One portion of the blende is decomposed with hydrochloric acid, and the *insoluble residue* is separated. *Lead* is determined in the filtrate as sulphate. After removal of lead, the *copper* is precipitated by means of hydrogen sulphide from a strongly acid solution; the *cadmium* is then precipitated in a similar manner from a slightly acid solution. After removal of the copper and cadmium, the *iron* is precipitated by means of “cupferron,” and the *manganese* is then separated as dioxide. In the filtrate, the *zinc* is determined as zinc ammonium phosphate, or volumetrically.

Sulphide and *carbonate* are determined in separate portions of the mineral.

One of the difficulties in this analysis is the separation of cadmium and zinc. The procedure given here is suitable for a zinc blende containing only a small quantity of cadmium.

Separation into Soluble and Insoluble Portions.—Introduce a weighed portion (about 1 gram) of the finely powdered zinc blende into a conical flask, and moisten the powder with water. Add about 20 c.c. of concentrated hydrochloric acid, and close the flask loosely with a small funnel or glass bulb. Warm on the steam-bath until there is no further action, and then add from time to time a few drops of concentrated nitric acid. When the residue is white and when any sulphur has been brought into solution, add a further 10 c.c. of concentrated hydrochloric acid, and boil for five minutes. Filter the *hot* solution through a small filter paper and wash with a boiling solution of hydrochloric

acid (half water and half concentrated acid) in order to dissolve any lead sulphate. Wash the residue with hot water, and ignite it. Weigh, and report the result as "insoluble residue."

Determination of Lead.—Evaporate the solution to about 10 c.c., cool, add 3 c.c. of concentrated sulphuric acid, and evaporate on a gently heated sand-bath until dense fumes of sulphuric acid are evolved. Cool, dilute to about 100 c.c., and collect the precipitate of lead sulphate as described on p. 231. The precipitate must be thoroughly washed with dilute (normal) sulphuric acid before washing with alcohol. (Reject alcohol washings.)

Determination of Copper.—Evaporate the filtrate and washings from the lead sulphate until it begins to evolve fumes of sulphuric acid. Cool, add 20 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and saturate the solution with hydrogen sulphide. Filter, and wash with a mixture of equal volumes of concentrated hydrochloric acid and saturated hydrogen sulphide solution, observing the precautions against oxidation mentioned on p. 175. Convert the cupric sulphide into cuprous sulphide, and weigh.

Determination of Cadmium.—Evaporate the filtrate until fumes of sulphuric acid appear. Cool, add 5 c.c. of concentrated hydrochloric acid, and transfer the solution to a conical flask, using hydrogen sulphide solution to rinse the basin. Then add slowly, with constant stirring, hydrogen sulphide solution until the volume is increased to about 150 c.c. Saturate the solution with hydrogen sulphide, collect the cadmium sulphide, and convert it into sulphate as described on p. 214.

Determination of Iron.—Evaporate the filtrate from the cadmium sulphide to about 50 c.c. Transfer to a beaker, add 1 c.c. of concentrated nitric acid, boil to oxidise ferrous salt, and dilute to 100 c.c. Determine the iron by the "cupferron" method (p. 229), or by a double precipitation with ammonia in presence of ammonium chloride (add 2 grams) as described on p. 270.

Determination of Manganese.—In the filtrate from the iron precipitation, determine the manganese as described on p. 234.

Determination of Zinc.—After removal of manganese, determine the zinc as zinc ammonium phosphate (p. 263) or volumetrically (p. 136).

Determination of Sulphur.—Place a weighed portion (about 0.4 gram) of the *finely powdered* zinc blende in a 150 c.c. conical flask. Add 20 c.c. of a mixture of three parts concentrated nitric acid and one part concentrated hydrochloric acid, and immediately cool under the tap. After a few minutes, add two or three drops of bromine and warm very gently on the steam-bath until all the sulphur has been oxidised. Boil for five minutes, and then transfer to a porcelain basin, using concentrated hydrochloric acid to rinse the flask. Evaporate to dryness, add 5 c.c. of concentrated hydrochloric acid, and again evaporate to dryness. To the residue add 30 c.c. of water and 10 c.c. of concentrated hydrochloric acid, and warm in order to dissolve any lead sulphate. Filter, and wash with a little hot, dilute hydrochloric acid and then thoroughly with hot water. Determine the sulphate in the filtrate as described on p. 170.

Determination of Carbonate.—In a separate portion (2 to 5 grams) of the zinc blende, determine the amount of carbonate (p. 215). Two U-tubes, each containing a concentrated solution of copper sulphate, must be placed next to the reaction flask in order to absorb the hydrogen sulphide.

ANALYSIS OF PYROLUSITE OR OF MANGANITE.

Pyrolusite and manganite are the commonest ores of manganese. The former consists mainly of manganese dioxide, and the latter mainly of the hydrated oxide, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Traces of “gangue,” ferric oxide, and barium oxide are usually present in both minerals.

OUTLINE OF METHOD.—One portion of the mineral is extracted with hydrochloric acid, and the *insoluble residue* of silica, etc., separated. *Barium* is separated as barium sulphate, and the *iron* is then precipitated by means of “cupferron” or by the basic acetate method. After removal of iron, the *manganese* is determined as manganese dioxide.

In another portion of the mineral, the *manganese dioxide* is determined by a volumetric method.

Water is determined in a separate portion of the mineral.

Determination of Barium, Iron, and Manganese.

To a weighed portion (about 0.5 gram) of the finely powdered mineral in a conical flask, add 10 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and close the flask loosely with a funnel or glass bulb in order to prevent loss by spirting. Warm on the steam-bath until the residue is white, and then evaporate to complete dryness in a porcelain basin. Moisten the dry residue with concentrated hydrochloric acid, set aside for five minutes, and then dilute to about 30 c.c. Filter through a small filter paper; wash the residue, and ignite it. Weigh, and report the result as "insoluble residue."

Determination of Barium.—Heat the filtrate until boiling, and to the hot solution add 1 c.c. of dilute sulphuric acid. Filter through a small filter paper, wash with hot water, incinerate the paper with the precipitate, and weigh the BaSO_4 . The quantity of barium in these minerals is so small, as a rule, that the error due to the retention of ferric oxide by the barium sulphate is negligible.

Determination of Iron.—Precipitate the iron in the filtrate by means of "cupferron," as described on p. 229. The separation from manganese of the small quantity of iron in these minerals may also be effected by a double precipitation of the iron with the minimum excess of ammonia in presence of much ammonium chloride (*cf.* p. 270), or by the basic acetate method (p. 203).

Determination of Manganese.—After the removal of iron, precipitate the manganese, together with any traces of calcium, etc., as carbonate (p. 233). Filter, and wash thoroughly. Perforate the filter paper with a glass rod, and, by means of a jet of water, wash the precipitate into a beaker. Cover the beaker with a clock-glass, and dissolve the crude manganous carbonate in dilute sulphuric acid; wash the filter paper with a little warm, dilute sulphuric acid in order to dissolve any traces of precipitate adhering to it, and add these washings to the main solution. Dilute the solution to about 200 c.c. and precipitate the manganese as dioxide (p. 234).

Determination of Manganese Dioxide.—In a separate

portion of the mineral determine the manganese dioxide by either of the methods described under volumetric analysis (pp. 82 and 113). If the amount of manganese found in this way is less than the total manganese as determined gravimetrically, calculate the excess of manganese, above that present as the dioxide, as MnO .

Determination of Water.—Determine the water in the mineral by Brush and Penfield's method (p. 261).

ANALYSIS OF SUPERPHOSPHATE MANURE.

Superphosphate manure is prepared from natural phosphate by treatment with sulphuric acid. By this treatment, insoluble tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is converted into soluble acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$. The value of a superphosphate as a plant fertiliser depends mainly on the amount of soluble phosphate present. It is therefore often sufficient to determine only the respective amounts of "soluble" and "insoluble" phosphates. The following scheme for a more complete examination of a superphosphate is sufficiently comprehensive for most purposes.

OUTLINE OF METHOD.—Separate portions of the superphosphate are used for the determination of (1) "Siliceous matter," iron, aluminium, and calcium; (2) Soluble phosphate; (3) Total phosphate; (4) Sulphate; (5) Water, organic matter, sodium and potassium; (6) Nitrogen.

The sample should be thoroughly mixed in order to secure uniformity, but it should not be dried or ground. All results should be expressed in percentages of the original, undried material.

Determination of Iron, Aluminium, and Calcium.

Place about 2.5 grams (accurately weighed) of the superphosphate in a porcelain basin, add 20 c.c. of water, 10 c.c. of concentrated hydrochloric acid, and 1 c.c. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness, first on the steam-bath and then on a *gently heated* sand-bath. Add 5 c.c. of con-

centrated hydrochloric acid to the dry residue and warm gently; then add 30 c.c. of water and heat for a few minutes. Filter, wash the insoluble residue with hot, dilute hydrochloric acid and then thoroughly with hot water. Ignite, and weigh the "insoluble residue."

Add sodium carbonate to the filtrate until it is alkaline (avoid loss due to effervescence), then add a few crystals of potassium nitrate and evaporate to dryness in a porcelain basin. Ignite the residue gently in order to destroy organic matter. Allow to cool. Dissolve the residue by warming with 10 c.c. of concentrated hydrochloric acid diluted with 30 c.c. of water. Transfer the solution (after filtering if necessary) to a 250 c.c. standard flask, cool, and dilute to the mark.

Determination of Iron and Aluminium.—(a) Measure 50 c.c. of the solution into a 600 c.c. beaker, add 10 grams of ammonium chloride, 2 c.c. of methyl orange, and ammonia until alkaline. Then add dilute hydrochloric acid, drop by drop, until just acid. Dilute to about 400 c.c., heat until boiling, add 3 grams of ammonium acetate, and boil for two minutes. Filter, and wash with a little hot water. Dissolve the precipitate in hot, dilute hydrochloric acid, and receive the solution in the original beaker. Wash the filter paper. Add 10 grams of ammonium chloride to the solution, neutralise the excess of acid as before, dilute to 300 c.c., and reprecipitate with ammonium acetate. Filter and wash with hot, 2 per cent. ammonium acetate solution. Incinerate the paper, and ignite the precipitate in an open crucible with a Méker burner. Weigh the mixture of FePO_4 and AlPO_4 .

(b) In another portion (100 c.c.) of the solution determine the iron volumetrically. Reduce the ferric salt in a Jones reductor (p. 95) and titrate with 0.02N permanganate (*cf.* p. 92); or reduce with stannous chloride and titrate with 0.02N dichromate (p. 98).

Determination of Calcium.—Mix the filtrates from the two precipitations of iron and aluminium phosphates and (without evaporation) precipitate the calcium as oxalate by adding 2 grams of ammonium oxalate (but no ammonia) to the boiling solution. Filter, wash the precipitate, convert it into CaO or CaSO_4 , and weigh (p. 177).

Determination of Soluble and Total Phosphate.

Determination of Soluble Phosphate.—Place 5 grams of the superphosphate in a 500 c.c. measuring flask and add 400 c.c. of water. Shake vigorously by means of a shaking machine for thirty minutes. Dilute the solution to 500 c.c. and, after mixing, filter part of the turbid mixture. (Reject the first portion of the filtrate.) Determine the phosphate in 10 c.c. of the filtrate (corresponding to 0.1 gram of the superphosphate) by the molybdate method, either gravimetrically (p. 242) or volumetrically (p. 75).

Determination of Total Phosphate.—Place a weighed portion (about 2 grams) of the superphosphate in a porcelain basin, add 25 c.c. of water and 10 c.c. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness, first on the steam-bath, and then on a *gently* heated sand-bath. Add 5 c.c. of concentrated nitric acid to the residue and warm gently; then add 30 c.c. of water and heat for a few minutes. Filter, and wash the insoluble residue with hot, dilute nitric acid and then with hot water. Dilute the solution, after cooling, to 500 c.c. in a standard flask. Determine the phosphate in 25 c.c. of the solution by the molybdate method.

Insoluble Phosphate.—The difference between the total phosphate and the soluble phosphate (expressed as percentages of P_2O_5) gives the percentage of P_2O_5 present as insoluble phosphate.

Determination of Sulphate.

Extract a weighed portion (0.5 to 1 gram) of the superphosphate with hydrochloric acid, evaporate to dryness, and prepare a solution as described on p. 304. In the filtrate from the insoluble residue, determine the sulphate as described on p. 170.

Determination of Water, Organic Matter, Sodium, and Potassium.

Determination of Water.—Spread in a thin layer a weighed portion (2 to 5 grams) of the superphosphate in a platinum basin, and dry for five hours at 100° . Report the loss of weight as "moisture."

Place the dried sample in an air-oven, and dry at 160° to 170° until the weight is constant. Report the further loss of weight as "combined water."

Determination of Organic Matter.—To the dried residue, add saturated barium hydroxide solution, mixing thoroughly with a glass rod, until the solution is alkaline. Evaporate to dryness on the steam-bath, and dry at 160° to 170° until the weight is constant. Then heat on a sand-bath, gently at first, and finally for fifteen minutes to barely visible redness. Cool in a desiccator, and weigh. The loss of weight resulting from the ignition is the weight of the organic matter.

Determination of Sodium and Potassium.—If sodium and potassium are to be determined, it is convenient to use the residue after the above treatment. Proceed in the same manner as with the ignited mass obtained in the determination of the alkalis by the Lawrence Smith method (p. 289).

Determination of Nitrogen.

Determine the nitrogen in a weighed portion (2 to 5 grams) of the superphosphate by Kjeldahl's method (p. 381).

PART VII

GAS ANALYSIS

THE analysis of a gas is usually conducted in one or other of two ways.

(1) A measured volume of the gas is treated with a suitable absorbing-reagent and the change of volume noted, or

(2) A measured volume of the gas is treated with a suitable reagent, and the constituent thus absorbed is then determined in the reagent. This is the usual method for the determination of traces of one constituent, since large volumes of gas may be used; it is also the general method for gases that are readily soluble in water, such as sulphur dioxide.

In practice, gases are always measured in contact with mercury or water. The vapour pressure of mercury is so small at ordinary temperatures that it may be neglected except in the most exact work. The vapour pressure of water is much greater, and cannot be neglected in accurate work. As a rule a gas is measured in the moist state at the room temperature and at barometric pressure, and corrections are then applied to find the volume the gas would occupy in the dry state at 0° and 760 mm. If v is the observed volume of the gas, t its temperature, p the barometric pressure in mm., and w the vapour pressure of water at temperature t , the corrected volume, V , is found from the following equation:—

$$V = v \frac{(p-w) 273}{760(273+t)}$$

Technical Methods.—Analyses can be performed rapidly and with sufficient accuracy for many purposes by using apparatus (designed mainly by Hempel) with water as the

confining liquid. In these analyses the above-mentioned corrections are neglected, since the error introduced in this way is not larger than other errors inherent in the same methods. It is assumed, in fact, that the temperature and pressure remain constant during the analysis. Any variation in the barometric pressure that may occur during an analysis is usually negligible, but care is necessary if the temperature variation is to be kept within sufficiently narrow limits. Obviously, the temperature will alter if any of the apparatus is brought near a flame, or is exposed to direct sunlight. For the same reason the apparatus must be lifted by the support, and the glass parts must not be touched more than is necessary with the hands.

COLLECTION OF A SAMPLE OF GAS FOR ANALYSIS

If a large quantity of the gas is available, it is most convenient to fill a tube or other vessel by displacement of the air originally present, care being taken that the air is completely displaced.

When the quantity of gas is limited, the receiver must be filled with water or mercury which is then displaced by the gas. An inverted wash-bottle with a piece of rubber tubing and a screw-clip on each of the tubes may be used for the collection of a gas (Fig. 68). In the laboratory it is usually possible to collect the gas directly in the gas-burette (see p. 312).

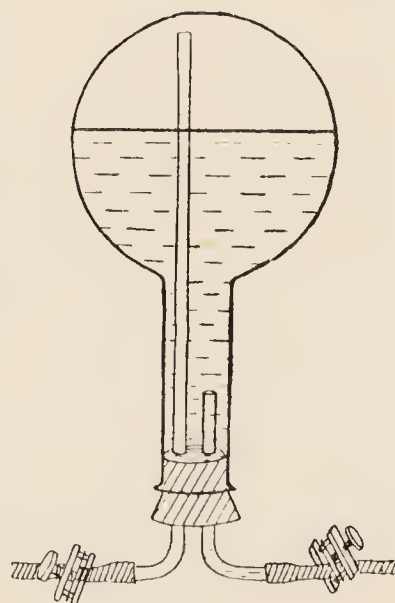


FIG. 68.

Samples of air in mines, etc., are conveniently collected in small (100 to 200 c.c.) glass-stoppered bottles. To collect the sample, remove the stopper, insert a rubber cork fitted with inlet and outlet tubes, and blow the air through the bottle by means of a small bellows or other simple air-pump. Withdraw the rubber cork, and immediately insert the glass stopper which is lubricated with vaseline to render the bottle air-tight. Fix the stopper in position by means of a stout

rubber band. The transference of the gas from the bottle to a gas-burette is described on p. 313.

In connection with both the collection and the analysis of a gas, two points require special mention, viz., the solubility of gases in water and aqueous solutions, and the permeability of rubber to gases. The solubility of nitrogen and oxygen is too small to affect an analysis seriously, particularly as the reagents are already saturated with these gases at their respective atmospheric partial pressures. With most other gases, the reagents should be saturated with each gas present in the mixture, at the pressure corresponding to its partial pressure. This is accomplished with sufficient exactness for most purposes by carrying out several successive analyses of the same sample; the error from this source will then diminish with each successive analysis, and the second or third analysis will be sufficiently accurate. Carbon dioxide, however, is so soluble that it cannot be accurately determined with any apparatus in which water is the confining liquid.

Since rubber is impermeable to water, one might presume that it would be impermeable to gases also, but this is by no means the case. All gases will pass through a rubber membrane even if it is free from flaws. The rate of diffusion through rubber varies with different gases, and is fast enough with carbon dioxide to introduce a serious error if the gas is exposed for any considerable time to a rubber wall. In practice, therefore, all rubber connections are kept as short as possible. Old or parched rubber should never be used, and all rubber tubes should be tested for leaks from time to time. Clips of any kind should be removed when the apparatus is not in use.

Gas Analysis with Hempel Apparatus

The sample of gas to be analysed is introduced into a gas-burette, in which it is measured. It is then led into a gas-pipette, in which it is treated with a reagent which absorbs one constituent of the mixture. The residue is brought back into the gas-burette and the volume again measured, the contraction giving the volume of the constituent absorbed. The residue is then led into another gas-pipette, where it is treated with another reagent which absorbs a second constituent, and the residual gas is again brought back to the burette for measurement. This series of operations is continued, using as many pipettes as there are constituents to be determined.

THE GAS-BURETTE.

This consists of a graduated measuring-tube M, and an ungraduated levelling-tube L (Fig. 69). Each tube is supported in an upright position by a stand, and the lower ends are connected by a rubber tube K of sufficient length to allow one tube to be placed on the floor while the other is on the working bench. The measuring-tube is graduated in fifths of a cubic centimetre, from 0 to 100 c.c. It terminates at the upper end in a short capillary tube to which a rubber tube R is attached. This rubber tube should be securely wired on to the glass capillary tube, leaving about 3 cm. of the rubber tube projecting.

To prepare the burette for an analysis, pour into the levelling-tube sufficient water to fill *one* of the glass tubes and the connecting rubber tube. In order to make sure that there is no air in the rubber tube, run the water to and fro in the tubes by alternately raising and lowering one of them. Then raise the levelling-tube until the measuring-tube and rubber tube R are completely filled with water,

and close the rubber tube with a clip, placed as near the glass as possible.

Introduction of a Sample into the Burette.—Fill the measuring-tube with water as described above, and close the clip on the tube R. If the rubber tube R is not quite full, fill it from a wash-bottle. Insert into the rubber tube a well-fitting, capillary-bored, glass tube leading from the vessel containing the gas to be analysed. All air in the leading-tube must have been previously expelled by passing some of the gas through it, or by filling it with water. Open the clip on the tube R and, by lowering the levelling-tube, allow the gas to enter until the burette contains a little more than 100 c.c. Close the clip on R, and disconnect the leading-tube.

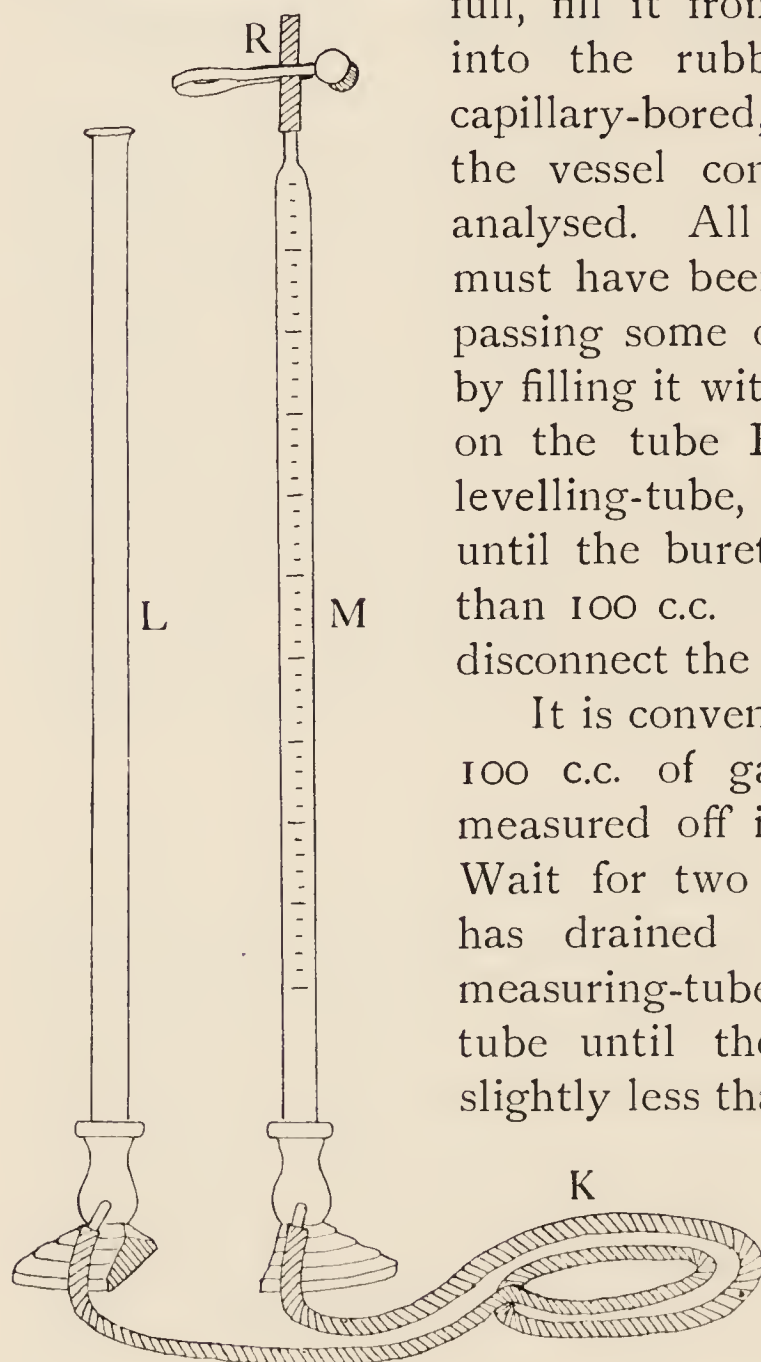


FIG. 69.

It is convenient to work with exactly 100 c.c. of gas, and this is readily measured off in the following manner. Wait for two minutes until the water has drained from the side of the measuring-tube, then raise the levelling-tube until the gas is compressed to slightly less than 100 c.c. and close the

rubber connecting-tube K by pinching between the fingers. Lower the levelling-tube and, by cautiously relaxing the pressure of the fingers

on the tube K, allow the gas to expand until the volume is exactly 100 c.c.; then pinch the rubber tube tightly again and open the clip on R for a moment. The excess of gas thereby escapes, leaving exactly 100 c.c. at atmospheric pressure. Make sure that the volume is exactly 100 c.c. by equalising the levels of the water in the two tubes of the burette and reading the volume of gas. When adjusting the water levels, hold the levelling-tube

in a sloping position and bring it into contact with the measuring-tube. The measuring-tube must be vertical.

The operation of introducing exactly 100 c.c. of gas into the burette should be practised with air.

Introduction of a Sample from a Small Bottle.—Hold the mouth of the bottle below the surface of some mercury contained in a deep trough. Remove the stopper, care

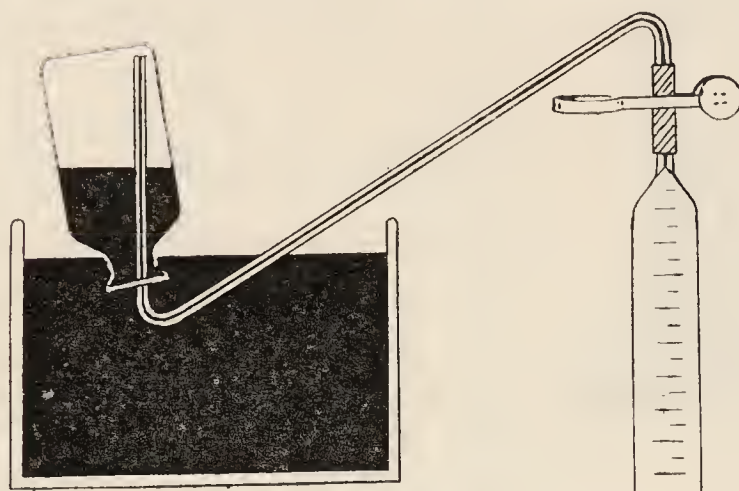


FIG. 70.

being taken that the mouth of the bottle is kept well below the surface of the mercury. Fill a bent, thick-walled, capillary tube with water, insert it into the bottle, and connect the other end of the capillary tube with the gas-burette (Fig. 70). The burette may then be filled as described above.

ABSORPTION PIPETTES.

Simple Absorption Pipette for Liquids.—This consists of two glass bulbs, A and B, connected by a wide tube. The bulb A is of about 150 c.c. capacity and is connected with a long capillary tube C, which is bent as shown in Fig. 71. The bulb B must not be less than 120 c.c. The pipette is supported on a suitable metal or wooden stand. A short piece of good rubber tubing is wired on to the open end of the capillary tube. When the pipette is not in use, this rubber tube should be closed with a glass plug, and the tube D should be closed with a small rubber stopper.

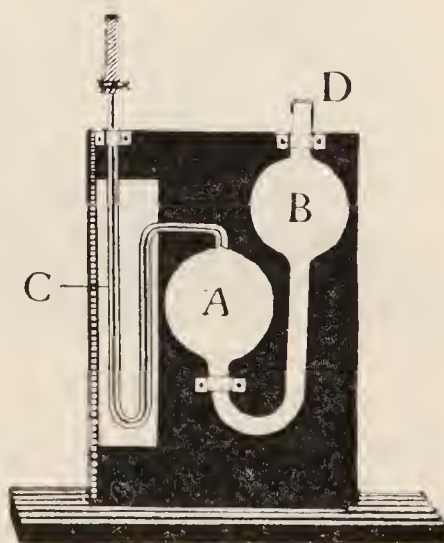


FIG. 71.

The pipette is filled by running in, through the tube D, sufficient of the reagent to fill the bulb A completely and the bulb B to a depth of about 1 cm.

Simple Absorption Pipette for Solids or Liquids.—This differs from the above form in having a tube at E (Fig. 72) through which a solid reagent may be introduced into the absorption bulb A. The tube E is closed with a rubber stopper which should be securely wired in place. With this pipette, absorption with liquid reagents can be greatly facilitated by packing the bulb A with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent. When the gas is then introduced into A, it is exposed to a large surface of the reagent.

Double Absorption Pipettes.—Reagents, such as cuprous chloride, alkaline pyrogallate, etc., which absorb oxygen, must not be used in the simple pipettes described above. With these reagents, a so-called “double pipette” (Figs. 73 and 74)

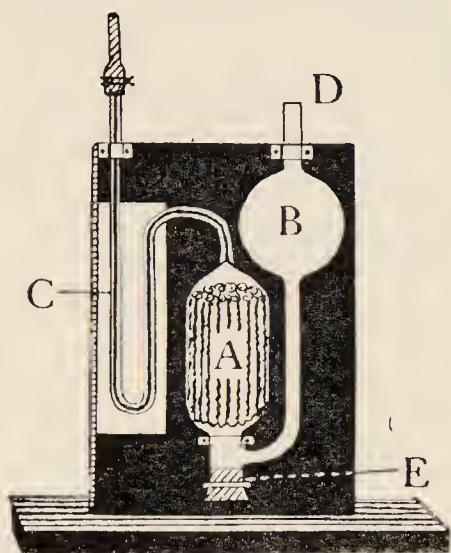


FIG. 72.

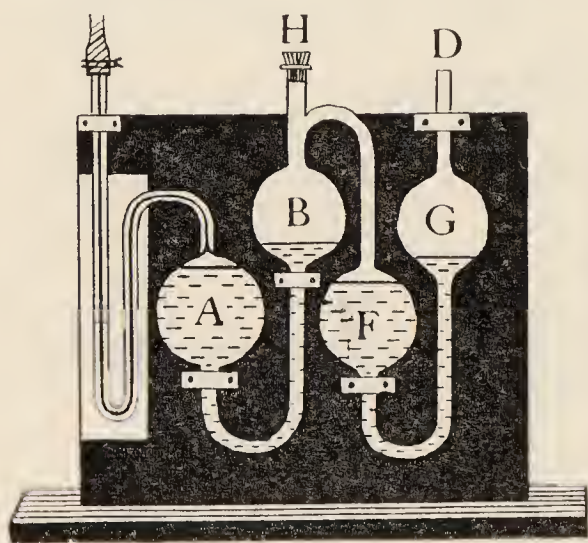


FIG. 73.

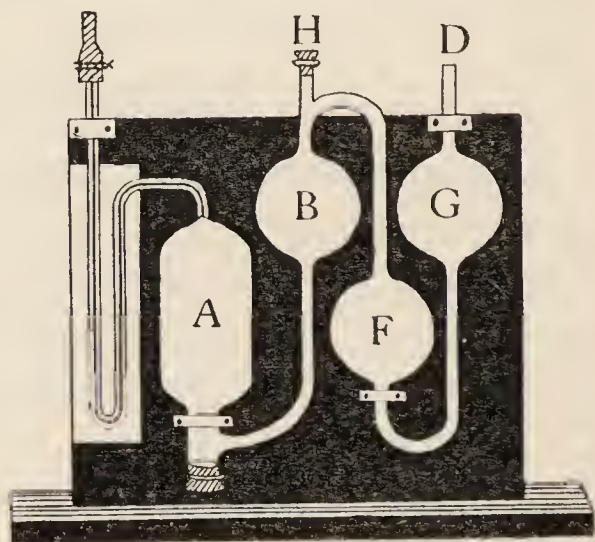


FIG. 74.

must be used. In this form of apparatus, the reagent in B comes into contact with an atmosphere free from oxygen, the indifferent gas being kept in place by water in the bulbs F and G.

The filling of a Hempel double pipette, as ordinarily constructed, offers some little difficulty. By the addition of

a side-tube, shown in the diagram at H, the pipette is as easily filled as a simple pipette. The pipette is first filled with an indifferent gas, such as nitrogen or hydrogen, by passing it through while the tube H is closed with a cork. The reagent is introduced by pouring it in through the tube H, and water is poured in through D until the bulb F is almost full—in order to form a water-seal. The tube H is then closed with a well-fitting rubber cork.

REAGENTS USED IN ABSORPTION PIPETTES.

Potassium Hydroxide. (*For carbon dioxide.*)—Dissolve 500 grams (or the contents of a 1 lb. bottle) in 1 litre of water, and store in a bottle with a rubber stopper. Pack the absorption bulb of a simple pipette (Fig. 72) with rolls of iron wire gauze of wide mesh and fill with the above solution of potassium hydroxide. When wet with this solution, the iron does not take up any oxygen by oxidation. Absorption of carbon dioxide in this pipette is usually complete in less than a minute.

One c.c. of the reagent will effectively absorb about 40 c.c. of carbon dioxide.

Bromine. (*For ethylene and other unsaturated hydrocarbons, and benzene.*)—Fill a double pipette (Fig. 73) with a saturated aqueous solution of bromine, and pour in a few cubic centimetres of liquid bromine to ensure that the solution remains saturated.

After the gas has been in contact with the reagent in the pipette for five minutes, draw it back into the burette, and then pass it into a potassium hydroxide pipette in order to remove bromine vapour; finally, return the gas to the burette, and measure it.

Fuming Sulphuric Acid. (*For ethylene and other unsaturated hydrocarbons, and benzene.*)—This reagent absorbs the same gases as bromine. A simple pipette, filled with glass beads or rods, may be used, but the special form with three bulbs, shown in Fig. 75, is recommended. The pipette is filled as usual, but great care must be taken that the reagent does not come into contact with the rubber connections or with water. The connecting-tubes must not

be filled with water, and, when the gas is transferred to the pipette, care must be taken to prevent any water passing over into the pipette. The absorption is complete within five

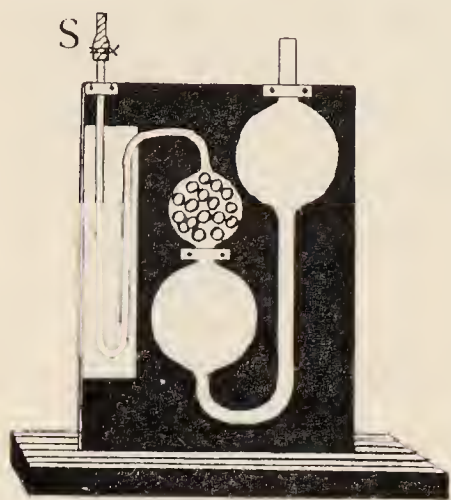


FIG. 75.

minutes. When the gas is withdrawn for measurement, allow the fuming sulphuric acid to follow until it reaches a mark made on the pipette capillary, showing the position of the reagent at the start of the experiment. (It is evident that an error is introduced on account of the air in the capillary. If the volume is known, a correction may be applied, but for many purposes the error is negligible;

in any case the error affects only the oxygen and nitrogen determinations to any appreciable extent.) As fuming sulphuric acid has a high vapour pressure, acid vapour must then be removed from the gas by passing it into a potassium hydroxide pipette before measurement.

The pipette must be refilled after about 1 litre of ethylene has been absorbed.

Alkaline Pyrogallate. (*For oxygen.*)—Dissolve separately 7 grams of pyrogallol in 25 c.c. of water, and 50 grams of potassium hydroxide in 110 c.c. of water. Mix the two solutions and introduce *at once* into a double pipette. Potassium hydroxide purified by alcohol must not be used.

The reagent absorbs oxygen very slowly at temperatures below 10° , but the absorption is rapid and complete at higher temperatures. The pipette must be refilled after about 200 c.c. of oxygen has been absorbed. The reagent will absorb oxygen in presence of ethylene, ammonia, and other substances that interfere with the absorption of oxygen by phosphorus.

Phosphorus. (*For oxygen.*)—Ordinary yellow phosphorus is cast in thin sticks¹ with which the bulb of a simple pipette

¹ To obtain fine sticks of phosphorus, melt it under water at about 50° in a narrow beaker, using enough phosphorus to fill the beaker to a depth of 6 or 7 cm. Dip a narrow glass tube into the molten phosphorus, close the top of the tube with the finger, and plunge the tube into cold water. The solidified phosphorus is readily removed.

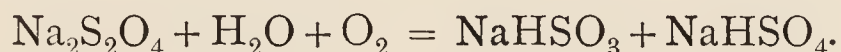
(Fig. 72) is packed. The pipette is filled with water, and the bulb is covered with a metal cover to protect the phosphorus from the action of light.

Absorption of oxygen is marked by the appearance of white clouds of the oxide, and is complete within five minutes if the temperature is above 15° ; at lower temperatures the absorption is much slower, and in cold weather sometimes does not occur at all unless the water in the pipette is warmed.

No absorption of oxygen takes place if the partial pressure of the oxygen is greater than about 0.5 atmosphere, or if the mixture contains ethylene, heavy hydrocarbons, ammonia, or alcohol, even in traces. A mixture containing above 50 per cent. of oxygen may be diluted with a known volume of nitrogen, and the oxygen will then be absorbed.

Phosphorus is much cleaner to work with than alkaline pyrogallate, and the pipette can be used for scores of analyses. The water must be changed from time to time.

Sodium Hydrosulphite. (*For oxygen.*)—Dissolve 25 grams of sodium hydrosulphite in 120 c.c. of water and add 30 c.c. of 50 per cent. sodium hydroxide. Introduce the solution at once into a double pipette. The reaction that occurs in the absorption of oxygen is represented by the equation—



The absorption is complete within five minutes even at low temperatures, and is unaffected by ethylene, ammonia, etc. The pipette should be refilled after about 300 c.c. of oxygen has been absorbed.

Ammoniacal Cuprous Chloride. (*For carbon monoxide.*)—Dissolve 15 grams of cuprous chloride and 10 grams of ammonium chloride in the minimum quantity of concentrated ammonia solution, and dilute to 200 c.c. Transfer the solution at once to a double pipette filled with rolls of copper gauze.

This reagent is used for the absorption of carbon monoxide, but, as it also absorbs carbon dioxide, oxygen, and ethylene, these gases must have been previously removed. Carbon monoxide forms with the reagent a compound having an appreciable dissociation pressure, and it is therefore necessary to pass the gas through two pipettes; the first may contain a

reagent that has been used several times, but the reagent in the second pipette should be as fresh as possible. The gas and the reagent *must* be brought into intimate contact by shaking (see below). Before measuring, the gas must be passed into a pipette filled with dilute sulphuric acid in order to remove the ammonia that escapes from the reagent.

MANIPULATION OF APPARATUS.

Introduce the sample of gas into the burette in the manner already described. Clamp the burette to a pipette stand as shown at P in Fig. 76. Fill the rubber tube R with water and insert the capillary tube N as close to the clip as possible. (The tube N should become filled with water.) Blow through D by means of an attached rubber tube until the capillary C and the rubber tube S become filled with liquid; then insert N and push it down until the glass tubes touch within the rubber junction. (The capillary tubes N and C should now be almost, if not entirely, free from air; if an air column longer than 1 cm. is enclosed, the above operations must be repeated more carefully.)

Measure the volume of the gas sample contained in the burette—say v_1 . Raise the levelling-tube, and open the clip on R *very cautiously* so that the gas enters the capillary N and drives the water over to a definite mark made on N just above the rubber tube S. Close the clip on R, equalise the levels, and read the burette again—say v_2 . (The difference between v_1 and v_2 , *i.e.* the volume of the capillary N, is usually about 0.2 c.c.) Then raise L, open the clip on R, and drive the gas into the absorption pipette until water from the burette begins to flow into the bulb A by the capillary C, and close the clip on R. Bring the gas into intimate contact with the reagent by rocking the whole apparatus gently *backwards and forwards*. (Shaking is unnecessary with a potassium hydroxide pipette containing wire gauze, or with a solid reagent such as phosphorus, on account of the large surface exposed to the gas.)

After shaking for five minutes, raise L and open the clip on R so as to rinse the end of the capillary C (where it joins A) with clean water from the burette. Lower L, the clip

on R being open, and bring the gas back into the burette until the reagent reaches the mark above the rubber tube S. Roughly equalise the levels, close the clip on R, and allow two minutes for the water to drain from the side of the burette. Equalise the levels and read the new volume of the

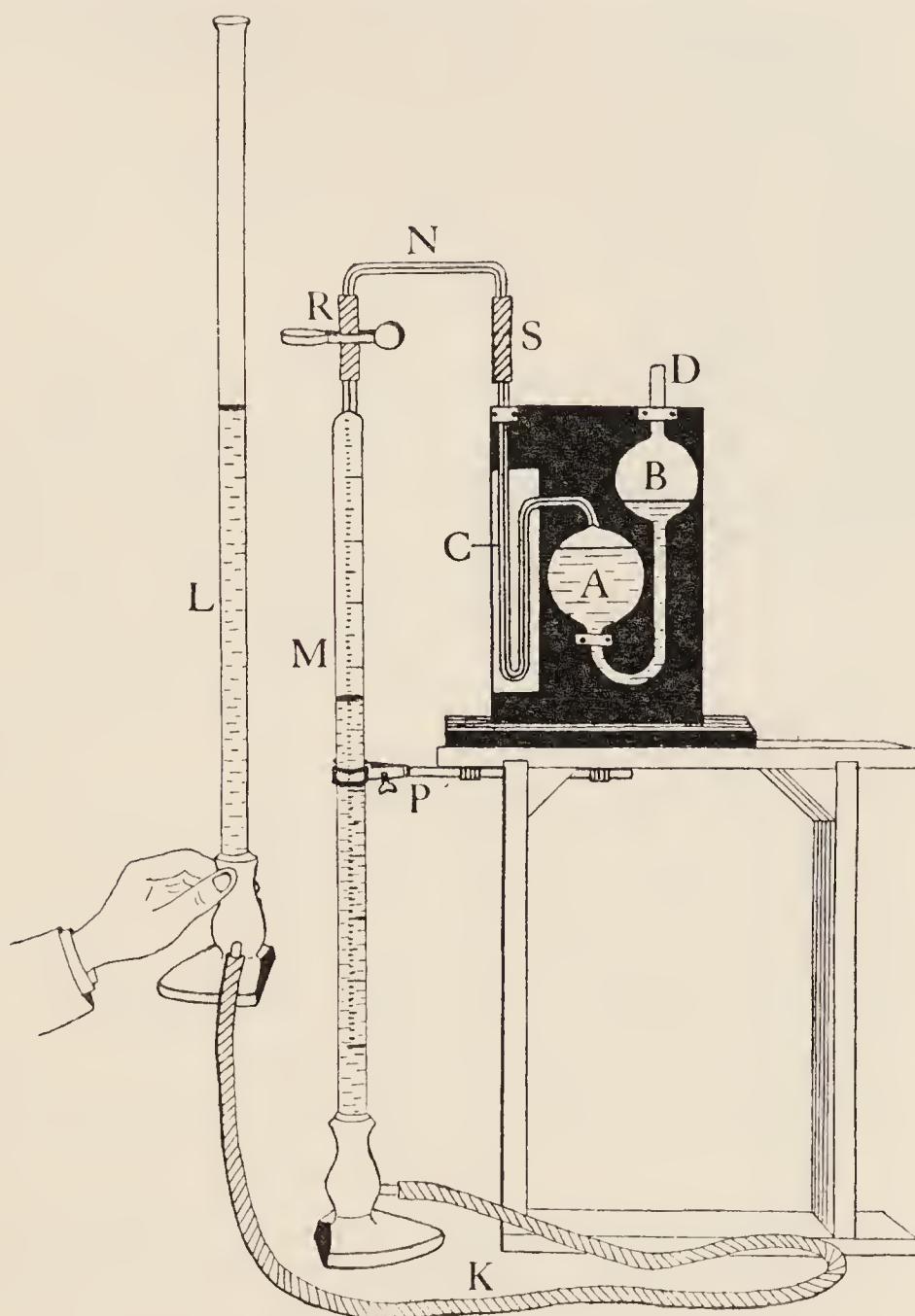


FIG. 76.

gas. Repeat the operations—by passing the gas into the pipette again and back into the burette for measurement—until a constant value for the new volume (v_3) is obtained. Absorption is then complete. The difference between the second reading (v_2) and the last reading (v_3) gives the volume of gas absorbed; and if the original volume (v_1) of the gas was 100 c.c., the difference in cubic centimetres is the percentage of the constituent in the mixture.

In order to determine the amount of a second constituent in the mixture, the original pipette with its rubber tube S is removed, the clip on R being, of course, closed; only a very small amount of reagent remains in the end of the tube N and serves to seal the capillary. A second pipette is then attached to N as before, and, the volume of the gas having been already measured to the mark on N, the absorption of the second constituent may be at once begun.

The final (true) volume of the residual gas may be found by adding the correction for the capillary N (usually about 0.2 c.c.) to the volume last observed.

ANALYSIS OF A GASEOUS MIXTURE.

In the analysis of a gaseous mixture, the gases must be determined in a definite order. The order in which the reagents *must* be used is given below for a mixture of the commoner gases; if a gas is known to be absent, the corresponding reagent will of course be omitted.

- | | |
|--|---|
| I. Potassium hydroxide | <i>for carbon dioxide.</i> |
| II. (a) Bromine; or (b) Fuming sulphuric acid (followed in either case by potassium hydroxide) | } <i>for ethylene.</i> |
| III. (a) Sodium hydrosulphite; or (b) Phosphorus; or (c) Alkaline pyrogallate | |
| IV. Ammoniacal cuprous chloride (followed by dilute sulphuric acid) | } <i>for carbon monoxide.</i> |
| V. The unabsorbed residue is analysed as described below | |
| | } <i>for methane, hydrogen, and nitrogen.</i> |

Analysis of a Mixture of Methane, Hydrogen, and Nitrogen.

OUTLINE OF METHOD.—After removal of all other gases, the methane and hydrogen are burned in a measured volume of oxygen. The products of combustion are removed, the contraction in volume is noted, and the amount of unused oxygen is determined. From the data obtained, the amounts of methane and hydrogen can be calculated. The residue is nitrogen.

Procedure.—Other gases are removed in the usual manner. The residue of methane, hydrogen, and nitrogen

is transferred to a slow-combustion pipette (Fig. 77) in which the methane and hydrogen are burned by admitting a slow stream of oxygen, the necessary heat being supplied by an electrically heated, platinum spiral. The spiral, which should be situated about 1 cm. from the top of the bulb, is heated to *dull redness* by means of a current from a 4- to 6-volt accumulator. An adjustable resistance is required for regulating the current.

Pass the gas into the pipette and see that the capillary is completely filled with water. Close the rubber tube on the pipette with a screw-clip, disconnect from the burette, and connect with a second burette containing exactly 100 c.c. of oxygen.¹

After starting the heating current, raise the levelling-tube, place it on a tall stand, and open the screw-clip cautiously so that oxygen is driven *very slowly* into the pipette—at the rate of about 5 c.c. per minute. (If the oxygen enters more rapidly, an explosion may occur.) During the combustion the spiral glows more brightly and the current must be regulated so that the wire is not heated much above dull redness. While combustion is in progress, the volume of gas in the pipette will contract; when combustion is complete, the volume will steadily expand. After a decided excess of oxygen has been added, close the clip on the pipette and continue to heat the spiral for two or three minutes.

Pass the gas into the burette and then, without previous measurement, into a potassium hydroxide pipette, in order to remove the carbon dioxide formed by the combustion of the methane. Return the gas to the burette and measure the

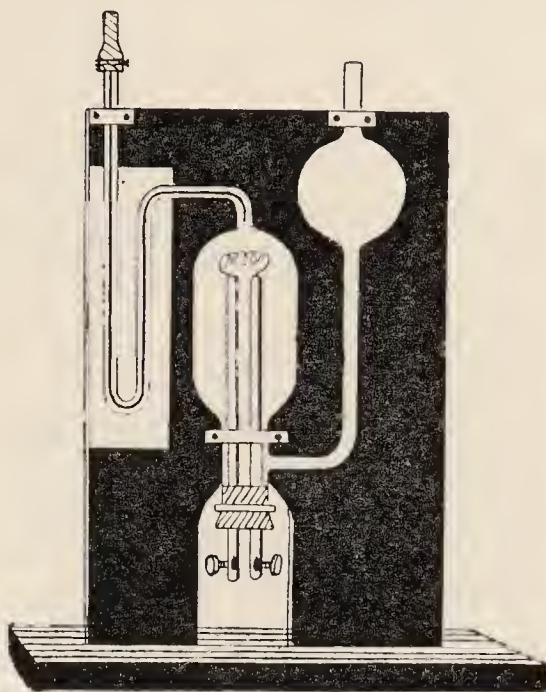
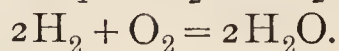


FIG. 77.

¹ Pure oxygen may be prepared by heating potassium permanganate in a hard glass test-tube. The oxygen is collected in a gas-holder and stored till required. It should be analysed and a correction applied if it contains any nitrogen.

volume. Absorb the excess of oxygen with phosphorus or sodium hydrosulphite, and measure the residue.

The reactions that occur in the combustion are—



If x be the volume of methane in the mixture, the volume of oxygen required for its combustion is $2x$; and if y be the volume of hydrogen, the volume of oxygen required for its combustion is $\frac{y}{2}$.

After combustion, the water and carbon dioxide are absorbed by the reagents. The contraction in volume resulting from the combustion of methane is three times the volume of the methane, *i.e.*, $3x$; and the contraction resulting from the combustion of hydrogen is one and a half times the volume of the hydrogen, *i.e.*, $\frac{3y}{2}$.

We have therefore :—

(1) The volume of oxygen used in the combustion

$$= 2x + \frac{y}{2}.$$

(2) The contraction in volume on combustion

$$= 3x + \frac{3y}{2}.$$

From these two equations, the quantities of methane and hydrogen are calculated.

The final unabsorbed residue is nitrogen, which, after correction for any nitrogen introduced with the oxygen, gives the quantity of nitrogen in the original mixture. This volume is, of course, the same as that obtained by subtracting the total of all the other constituents from the original volume.

There is no simple method for the direct determination of nitrogen.

Analyses Involving the Use of a Lunge Nitrometer

The Lunge nitrometer (Fig. 78) consists of two glass tubes connected by a stout rubber tube. The levelling-tube L is ungraduated and is open to the air; the measuring-tube M is graduated and is fitted at the top with a three-way tap, so that the measuring-tube may be connected with either the cup C or the tube A. By means of this tap a sample of gas may be drawn into the apparatus through the tube A, and then, by turning the tap, any desired reagent may be run in from the cup C. The pressure tubing used to connect the two glass tubes should be a little longer than the measuring-tube, and must be securely wired on to the tubes.

At all times the apparatus should stand on a mercury tray. Special clamps with wide grips may be obtained for holding the apparatus, but *good* burette clamps, with rubber pads on the grips, are quite satisfactory. Each tube, when filled with mercury, weighs about 3 lb., and the use of a flimsy burette clamp means the almost certain breakage of the apparatus.

Nitrogen in a Nitrate or Nitrite.

OUTLINE OF METHOD.—The nitrate or nitrite is reduced to nitric oxide by shaking with mercury and concentrated sulphuric acid in the measuring-tube of a Lunge nitrometer. The nitric oxide is measured, and, from the volume of nitric oxide, the weight of nitrogen is calculated.

Procedure.—The solution containing the nitrate should not exceed 2 c.c. in volume; if necessary, it must be evaporated until reduced to this volume.

Fill the measuring-tube of the nitrometer with mercury by raising the levelling-tube. Pour the nitrate solution into the cup C. By cautiously opening the tap, run the solution

into the nitrometer without admission of any air. Wash out the vessel that contained the nitrate *with a few drops* of dilute sulphuric acid, and run this in through the cup in a

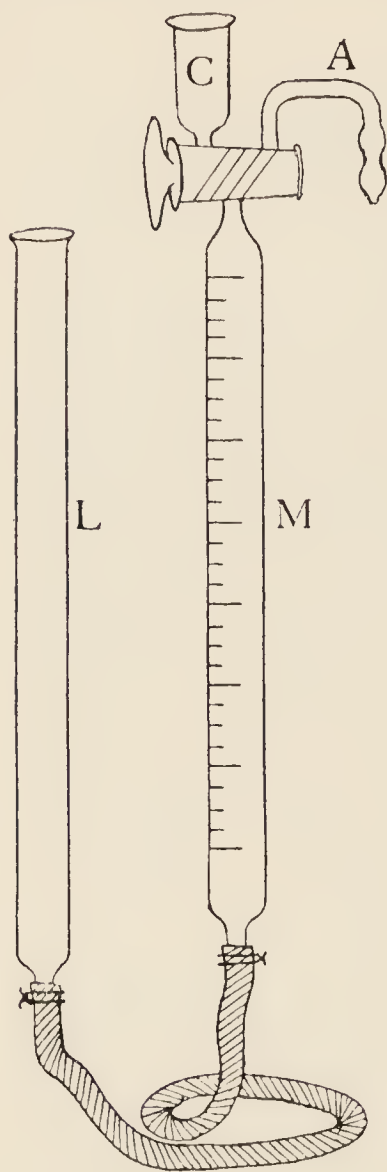


FIG. 78.

similar manner. (Keep the volume of liquid and washings as small as possible—the total should not in any case exceed 4 c.c.) Pour about 15 c.c. of concentrated sulphuric acid into the cup and run this into the nitrometer, care being taken that no air is admitted. Remove the measuring-tube from the clamp and shake with a rotary motion, so that globules of mercury are thrown up into the liquid. In a minute or two the evolution of nitric oxide will begin. If no gas appears after shaking vigorously for 2 to 3 minutes, cautiously run in a few drops of water and shake again. The shaking must be continued until the evolution of nitric oxide ceases. Allow the apparatus to assume the room temperature, and then measure the volume of the gas under atmospheric pressure.

In order to adjust the pressure, assume the density of the aqueous liquid to be one-eighth that of mercury, and clamp the levelling-tube in the appropriate

position. If the adjustment is correct, it will be found that a drop of liquid in the nitrometer cup is neither drawn in nor forced out when the tap is *very cautiously* opened. Care must be taken not to warm the gas by handling the measuring-tube.

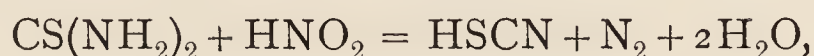
The temperature and the barometric pressure must be noted and the observed volume reduced to N.T.P. One c.c. of nitric oxide at 0° and 760 mm. weighs 0.001340 gram, and corresponds to 0.000626 gram of nitrogen.

At the conclusion of an experiment, the measuring-tube may be readily cleaned by rinsing it three times with concentrated sulphuric acid, using 5 c.c. each time.

Exercise.—Determine the percentage of nitrogen in potassium nitrate. Use about 0.2 gram.

Nitrite.

When a nitrite is added to an acid solution of thiourea, the reaction that follows depends on the strength of the acid. In presence of a weak acid, such as acetic acid, the chemical change takes place almost entirely in accordance with the equation—



whilst if hydrochloric acid is present, the interaction may be represented by the following equation—



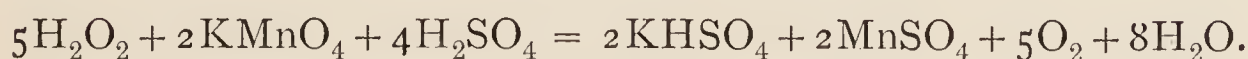
In the first case, a little nitric oxide is always obtained, and in the second case a little nitrogen, but this does not affect the determination since the volume of gas obtained is the same in both cases. On account of the lower solubility of nitrogen, it is preferable to use acetic acid.

Procedure.—Weigh accurately about 0.15 gram of sodium nitrite. Introduce the weighed sample, together with about 0.2 gram of thiourea, into the cup of the nitrometer, and dissolve in 1 to 2 c.c. of water. Run the solution into the measuring-tube and rinse the cup with *a few drops* of water. Then introduce 1 c.c. of 50 per cent. acetic acid, and shake vigorously.

Gas is evolved immediately the solution is acidified, and the reaction is complete in a few minutes. If the total volume of aqueous liquid is not greater than 4 c.c., the error due to the solubility of the gas in water is negligible.

Hydrogen Peroxide.

Hydrogen peroxide, in presence of sulphuric acid, interacts with potassium permanganate as follows :—



The concentration of a solution of hydrogen peroxide may therefore be determined by measuring the volume of oxygen obtained from a known volume of the peroxide solution on treatment with excess of permanganate.

The apparatus (Fig. 79) consists of a reaction vessel, together with a Lunge nitrometer. The reaction vessel consists of a small conical flask with a well-fitting rubber cork which carries a glass tube. Connection with the tube A

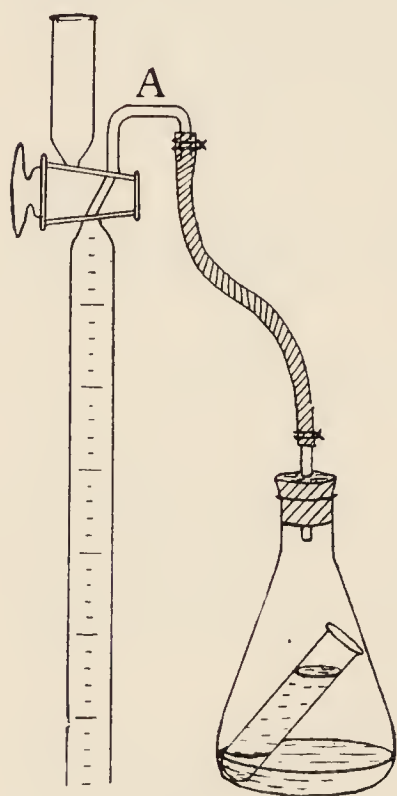


FIG. 79.

of a nitrometer is made by means of a piece of pressure tubing. A short wide test-tube is also required; this must be slightly longer than the base of the flask in order that, when placed in the flask, it will remain in the position shown in the diagram.

Procedure.—Place 20 c.c. of saturated potassium permanganate solution and 20 c.c. of dilute sulphuric acid in the conical flask. Dilute 10 c.c. of commercial hydrogen peroxide to 100 c.c., and place 10 c.c. of this diluted solution in the test-tube. Place the test-tube carefully in the flask, care being taken that no mixing of the peroxide and permanganate occurs

at this stage. Insert the rubber cork and connect the flask with the nitrometer, which is filled with mercury. Loosen the tap of the nitrometer in its socket, and place the conical flask, up to the neck, in water at the room temperature. After about five minutes, adjust the mercury to the zero mark, insert the tap firmly into position, and turn it so that the reaction vessel is in communication with the measuring-tube. If the mercury level alters in the course of a few minutes, the temperature is not yet constant.

When the temperature has become constant, tilt the reaction flask so that the peroxide solution mixes with the permanganate. Keep the pressure approximately equal to the atmospheric pressure by lowering the levelling-tube from time to time. Rinse out the small tube with some of the permanganate solution by appropriate manipulation of the flask. When the reaction is apparently complete, shake the flask vigorously. (The liquid, unless violently agitated, may retain several cubic centimetres of dissolved oxygen.)

Adjust the mercury levels and read the volume of oxygen.

Reduce the volume to N.T.P. and calculate the weight of hydrogen peroxide per litre of the original solution.

The concentration of hydrogen peroxide is commonly expressed in terms of the volume of oxygen obtained from it on decomposition by heat. Thus "ten volumes" hydrogen peroxide solution yields ten times its own volume of oxygen at room temperature. (It may be pointed out that double this volume of oxygen is obtained when the peroxide is treated with permanganate.) Calculate the concentration of the peroxide solution in this way also.

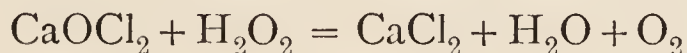
Valuation of Zinc Dust.

Zinc dust is frequently used as a reducing agent, and an estimate of its value for this purpose may be obtained by measuring the volume of hydrogen evolved when a weighed sample is treated with excess of acid.

Place about 0.1 gram (accurately weighed) of the sample in the conical flask (Fig. 79) and add 25 c.c. of water. In the small test-tube place 5 c.c. of concentrated sulphuric acid. Proceed as described in the determination of hydrogen peroxide. From the volume of hydrogen evolved, calculate the percentage of zinc in the zinc dust.

Available Chlorine in Bleaching Powder.

Bleaching powder and hydrogen peroxide interact as follows:—



One c.c. of oxygen at N.T.P. is equivalent to 0.00317 gram of available chlorine.

Measure into the conical flask (Fig. 79) 25 c.c. of a solution of the bleaching powder prepared as described on p. 115. In the small test-tube place 3 c.c. of "ten volumes" hydrogen peroxide. Proceed as described on p. 326. From the volume of oxygen evolved, calculate the percentage of available chlorine in the bleaching powder.

Determination of Gases present only in Traces

Methods depending on the alteration in volume produced by absorption are not suitable for the determination of traces of gases. An accuracy of 1 in 1000 in the measurement of a gas-volume is within the limits of what one would ordinarily regard as "permissible error." An illustration will make it clear that this error is far too large for many purposes. The amount of carbon dioxide in the atmosphere is usually about 3 parts in 10,000 or 0.03 per cent., and 0.03 c.c. would be the alteration in volume produced by absorption of the carbon dioxide in 100 c.c. of air. Even assuming that, by special precautions, the error of measurement were reduced to 1 in 10,000, there would still be an uncertainty of about 30 per cent. in the amount of carbon dioxide.

In practice, therefore, traces of gases are determined in a different manner. A large volume of the gas mixture is treated with a suitable absorbent, and the absorbed constituent is then determined by analysis of the reagent. For example, carbon dioxide in air may be determined by treating a large measured volume of air with a measured volume of standard baryta solution, and finding, by analysis, how much of the baryta has been converted into carbonate. The attainable accuracy is obviously greatly increased by the substitution of a chemical determination of the carbonate for the measurement of a minute alteration in a large volume. A comparatively rough measurement of the total volume is usually sufficiently accurate for a process of this kind.

Measurement of the Gas Mixture.—From the nature of the case, no general rules can be laid down. For the measurement of coal gas or other gas of which a large supply is available, a gas-meter is most convenient. The special

description of the determination of carbon dioxide in air (see p. 331) may suggest a method that could be adapted to other cases.

Absorption Apparatus.—Convenient forms of apparatus for holding the absorption reagent are shown in Fig. 80, A and B. If the gas contains dust, it must be passed through

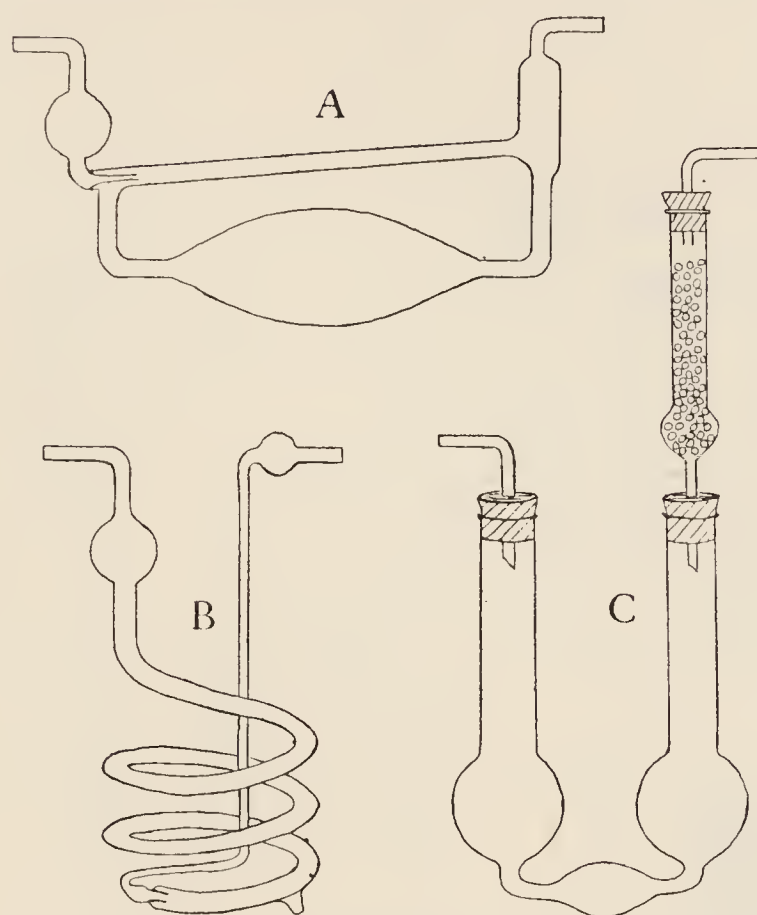


FIG. 80.

a tube packed with pumice or glass beads, moistened with the reagent (as in Fig. 80, C).

Sulphur in Coal Gas.

OUTLINE OF METHOD.—The coal gas is burned in air and the sulphur dioxide formed is absorbed by a solution of sodium carbonate and bromine. All the sulphur is thereby obtained as sodium sulphate, and the sulphate is determined gravimetrically in the ordinary manner.

The gas is measured by a gas-meter and is led by the tube A into the glass flask B (Fig. 81). This is a 1 litre, round-bottomed, hard-glass flask with a short, wide mouth. The inlet tube must be of hard glass, and is drawn to a fine jet at C where the gas is burned. The air required for the

combustion of the gas is freed from any traces of hydrogen sulphide in the laboratory atmosphere by passing it through the purifier E filled with pumice, upon which a concentrated solution of potassium hydroxide is constantly dropping

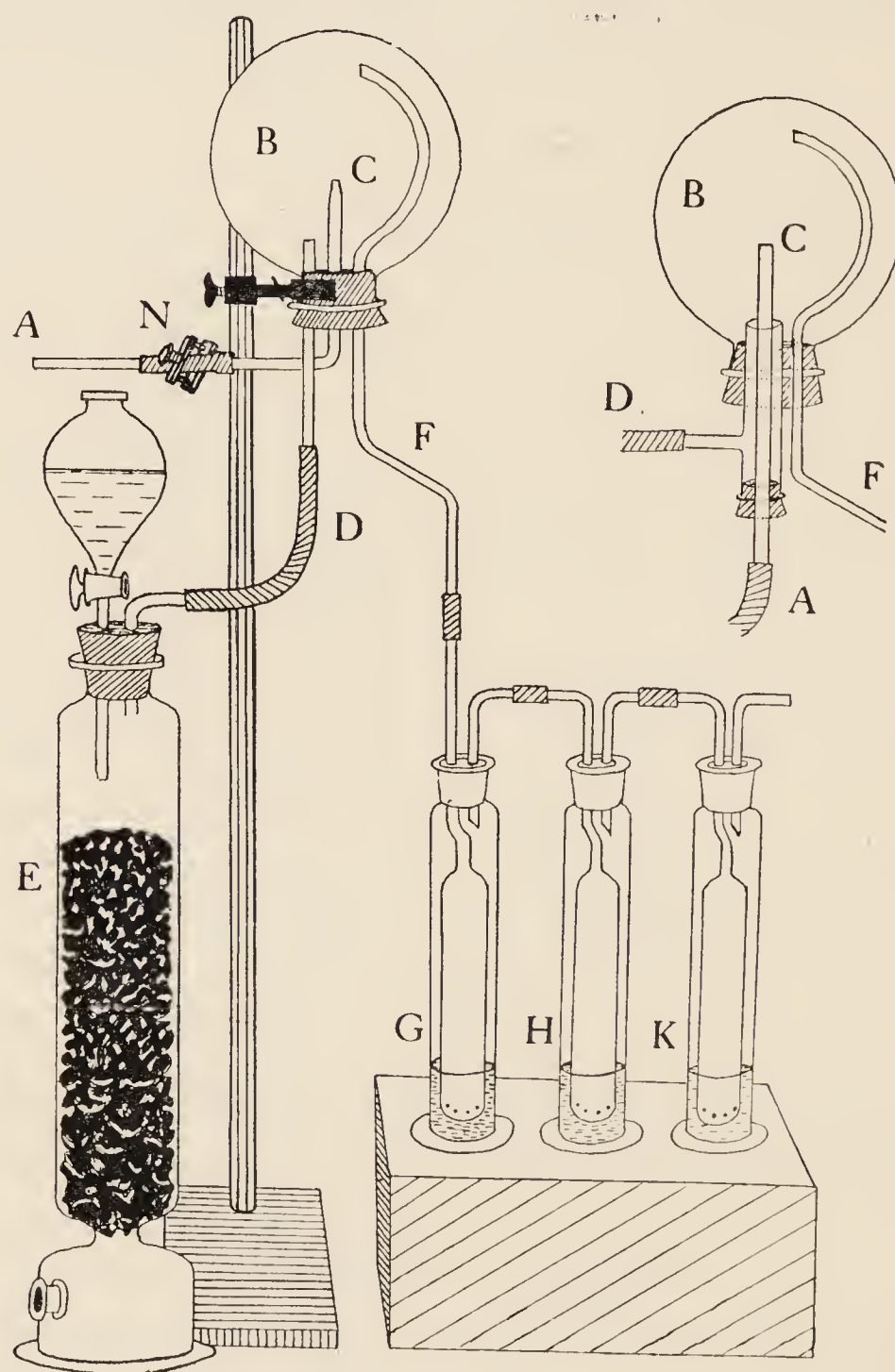


FIG. 81.

from a tap funnel. The purified air then passes by the tube D into the flask B. The products of the combustion are drawn out of the flask by means of a filter-pump through the tube F, and through three wash-bottles G, H, K, in which the sulphur dioxide is retained. The wash-bottles each contain sodium carbonate solution. To G and H a few drops of

bromine are also added in order to oxidise the sulphite to sulphate.

A larger, steady flame may be obtained by the modified arrangement of the gas and air supplies shown at the side of the diagram. The gas is led in through the central tube and the air through the outer tube.

Procedure.—Pass the coal gas through the meter for a few minutes, and draw a rapid current of air through the apparatus by means of a filter-pump. Withdraw the cork carrying the three tubes from the flask B, and ignite the gas at C. By means of the screw-clip N, cut down the gas supply until the flame is about 10 mm. high; then insert the cork in the flask. By regulation of the air and gas supplies, adjust the flame so that it burns with sharply defined edges.

When about 50 litres of gas have been burned, cut off the gas supply. Wash the contents of the wash-bottles G and H into a beaker, and rinse the flask B into the same beaker. Acidify the solution with hydrochloric acid, boil until the excess of bromine is expelled, and determine the sulphate gravimetrically as barium sulphate.

It is advisable to test the bromine used, because it sometimes contains sulphuric acid.

Atmospheric Carbon Dioxide.

OUTLINE OF METHOD.—The sample of air, contained in a dry bottle of known capacity, is shaken with a measured volume of standard baryta solution until the absorption of the carbon dioxide is complete. The precipitated barium carbonate is removed by filtration, and the excess of barium hydroxide is determined by titration with standard hydrochloric acid, these operations being conducted in such a way that the baryta is protected from expired air. The amount of carbon dioxide is calculated from the amount of baryta transformed into carbonate.

The following solutions are required:—

Decinormal Hydrochloric Acid.—Dilute 10 c.c. of concentrated hydrochloric acid to 1 litre and standardise by means of calcite, or by titration with standard baryta.

Fiftieth-normal Baryta.—Prepare as described on p. 64.

The Apparatus required is shown in Fig. 82. The absorption bottle C, of which several should be provided, is

a Winchester quart, the capacity of which has been previously determined. It is furnished with a rubber stopper, through which pass two tubes, the shorter tube being flush with the stopper inside the bottle. The tubes project 4 to 5 inches externally, and are provided with taps. The shorter tube is connected by means of a piece of narrow-bore rubber tubing, 8 inches long, with a filtering-tube (Fig. 82, F) containing an asbestos filter. This tube is fitted into a 200 c.c. filter-flask by means of a rubber stopper.

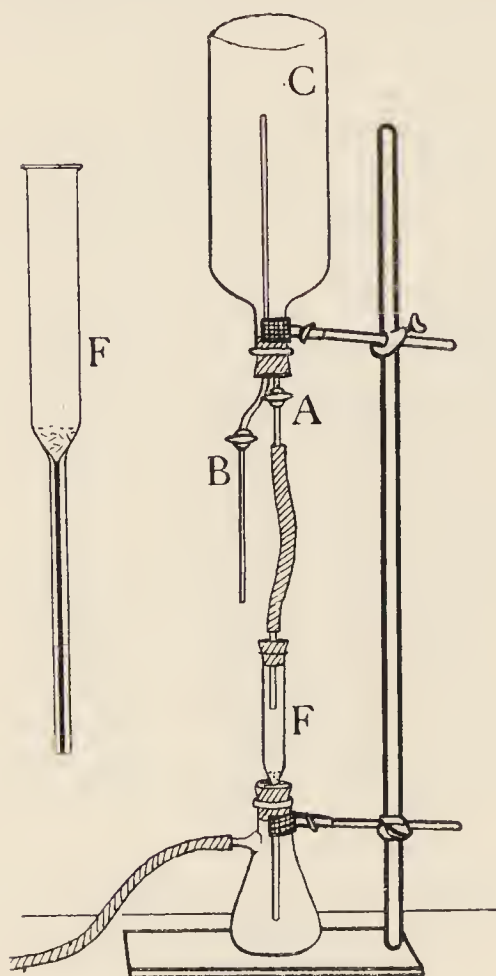


FIG. 82.

By means of bellows or a suction pump, fill the bottle with the air to be analysed, care being taken that expired air is not drawn directly into the bottle. Close the bottle with the rubber stopper and tubes, or with a glass stopper smeared with a trace of grease. Note the temperature at the time of collection. (The error that may be introduced by assuming that the pressure is 760 mm. is less than other errors inherent in the method.)

Collecting the Sample. — By means of bellows or a suction pump, fill the bottle with the air to be analysed, care being taken that expired air is not drawn directly into the bottle. Close the bottle with the rubber stopper and tubes, or with a glass stopper smeared with a trace of grease. Note the temperature at the time of collection. (The error that may be introduced by assuming that the pressure is 760 mm. is less than other errors inherent in the method.)

Procedure.—If the absorption bottle has been closed with a glass stopper, replace the latter quickly *in the open air* by the rubber stopper and tubes, just before the analysis is carried out.

Insert the jet of the baryta burette into the longer tube, open the taps A and B, and run 50 c.c. of baryta into the bottle. Close the taps, wet the whole interior of the bottle with the baryta solution, lay the bottle on its side, and shake it at frequent intervals during fifteen to twenty minutes.

Meanwhile, prepare the asbestos filter by pushing a *small* plug of glass wool into the filtering-tube, and then pour into the tube a small quantity of the asbestos mixture used for Gooch crucibles. Connect the filter-flask with the pump and wash the filter several times with water. Then

empty the filter-flask and measure into it 10 c.c. of the standard hydrochloric acid. Prepare also a special solution for washing out the absorption bottle, by adding to 100 c.c. of distilled water (which always contains carbon dioxide) 2 c.c. of phenolphthalein, a little barium chloride, and then baryta solution until an incipient pink colour is produced. The purpose of the barium chloride is to diminish the solvent action of the water on the barium carbonate.

When the absorption is complete, fix the bottle in its clamp and connect with the filtering-tube. Start the filter-pump at a moderate speed and open tap A. Leave A open for about thirty seconds after the baryta has passed through the filter in order to exhaust the bottle partially, then close A.

Dip the end of tube B into the special washing solution contained in a small beaker, open B carefully, and allow about 20 c.c. to pass into the bottle, then close B. Remove the bottle from its clamp, hold it in a horizontal position, and, by rotating and shaking it, thoroughly rinse the whole interior. Replace the bottle in the clamp, allow the liquid to drain for a few seconds, and again open A.

Repeat these operations several times until the absence of colour in the washings shows that the baryta has been completely removed from the bottle. Now admit air to the apparatus, detach the filter-flask, pour the contents into a porcelain basin, and titrate with baryta until the solution is nearly neutral. Wash out the filter-flask with a portion of the nearly neutral liquid, and finish the titration.

Example—

1 c.c. baryta	= 0.2201 c.c. of CO ₂ at N.T.P.
10 c.c. hydrochloric acid	= 49.0 c.c. baryta.
Capacity of bottle	= 2650 c.c.

Fifty c.c. of baryta were placed in the bottle, and 10 c.c. of hydrochloric acid in the filter-flask. After absorption of the carbon dioxide, the acid remaining in the filter-flask required 3.0 c.c. of baryta to neutralise it.

Total baryta used = $50 + 3 = 53$ c.c.

But 10 c.c. acid neutralises 49.0 c.c. baryta.

Therefore the CO₂ neutralised $53 - 49 = 4$ c.c. baryta.

The volume of air was equal to $2650 - 50 = 2600$ c.c., and the temperature was 15°C .

The amount of carbon dioxide in the sample of air was therefore :—

$$\frac{4.0 \times 0.2201 \times 10,540}{2600} = 3.57 \text{ vols. of CO}_2 \text{ in 10,000 vols. of air.}$$

[10,540 volumes at 15° are equal to 10,000 volumes at 0° .]

If the sample of air was collected at a temperature greatly exceeding the temperature of the laboratory, a correction may be made for the amount of carbon dioxide that enters the bottle with the outdoor, atmospheric air (containing about 3 parts of carbon dioxide in 10,000) when the bottle is opened at the start of the analysis. For a temperature difference of 10° , the correction is approximately equivalent to a deduction of 0.1 volume of carbon dioxide in 10,000 volumes of air.

Hydrogen Sulphide in Coal Gas.

After measurement, the gas is dried by passing it over calcium chloride. The hydrogen sulphide is then absorbed by passing the gas through **U**-tubes containing pumice impregnated with copper sulphate and, at the exit end, a little calcium chloride. The pumice is prepared for use by soaking it in a hot, saturated copper sulphate solution and then drying it for four hours at 150° to 160° .

The increase in weight of the **U**-tubes gives the amount of hydrogen sulphide.

Sulphur Dioxide in Flue Gases.

A measured volume of the gas is drawn through a tube containing cotton wool to remove dust and then through a solution of sodium carbonate and bromine (see p. 330). The sulphate formed is determined gravimetrically.

PART VIII

WATER ANALYSIS

Pure and Natural Water.—Natural water is never ideally pure water. It always contains, in solution or suspension, inorganic and organic substances derived from the air, the soil, and the rocks with which it comes into contact; and it may have become polluted, directly or indirectly, with sewage or other waste products of human life and industry.

The substances that may be present in a natural water are chiefly (1) calcium, magnesium, and sodium salts, in the form of bicarbonate, chloride, sulphate, and nitrate; (2) comparatively small amounts, or traces, of iron and ammonium salts, nitrite, and phosphate; (3) dissolved gases—carbon dioxide, oxygen, and nitrogen; (4) dead organic matter, in solution or suspension; (5) living organisms, including bacteria.

Purpose of Water Analysis.—An examination of a water supply is generally made for the purpose of deciding whether the water is suitable for domestic or industrial purposes. In the case of a potable water, it is necessary to ascertain that the salts present are not objectionable, either as regards their nature or their amount, and that the water does not contain more than a mere trace of organic matter.

For washing and scouring, it is desirable to use what is familiarly known as a “soft” water, *i.e.* a water containing comparatively small amounts of calcium and magnesium salts. For steam-raising purposes, a soft, alkaline water, free from substances that produce hard scale, corrosion, or priming, has many advantages; and many important industries, such as brewing, paper-making, and dyeing, are dependent upon a satisfactory water supply. The water

best adapted for domestic use is equally suitable for many technical purposes; but the presence of certain salts may be desirable for one manufacturing process and objectionable for another.

Methods of Examination.

The investigation of a water supply includes an examination of (1) the source from which the water is derived; and (2) the water itself. The two main sources of water suitable for general purposes are:—

- (a) Ground Water, *i.e.* wells and springs.
- (b) Surface Water, *i.e.* streams and rivers.

The Examination of the Source of the supply is directed mainly to the detection of pollution or of possible sources of pollution. The importance of this examination lies in the fact that a water supply, although satisfactory as a rule, may be liable to *occasional* pollution which an analysis of the water itself may fail to disclose. A careful inspection of the source may, in fact, render a complete analysis of the water almost superfluous, and it will, in any case, assist in the correct interpretation of the analytical results.

Shallow wells are often liable to pollution, on account of either their position or their unsatisfactory construction. It may be possible to remove the source of pollution, or to prevent the impurity reaching the well. In the case of river water, pollution—either from sewage or other waste products draining into the river, or from cultivated land through which the river flows—is almost inevitable, and river water must always be purified by storage and efficient filtration before it can form a satisfactory water supply for household purposes.

The Examination of the Water comprises (1) a physical and chemical examination; (2) a microscopical examination; and (3) a bacteriological examination.

In what follows, only the physical and chemical methods of examination will be considered.

Physical and Chemical Methods of Examination and Analysis

When a water supply is intended for a drinking water, it is usually desirable to make a comprehensive investigation, involving most of the qualitative and quantitative determinations described below. If the water is to be used for industrial purposes, a more restricted examination will generally suffice—the chief constituents of importance in that case being the bicarbonates, sulphates, and chlorides of calcium and magnesium.

The results of the quantitative determinations are usually expressed in parts per 100,000 of water which, it may be noted, correspond to milligrams per 100 c.c.¹

COLLECTION OF SAMPLES OF WATER.

At least 2 litres of water are required for a fairly complete analysis. Samples are most conveniently collected in Winchester. The bottles should be of light-coloured glass. Before being used for samples, the bottles must be carefully rinsed with water, and should be filled completely with the rinsing water at least once. Bottles intended for holding water samples should be reserved for that purpose alone. For convenience and safety during transport, the bottles may be placed upright in wicker baskets or in padded boxes made for the purpose.

If the sample is to be collected from a tap, the water should be allowed to run to waste for several minutes before filling the bottle. In taking a sample from a river, loch,

¹ Results are sometimes given in grains per gallon ; to convert them into parts per 100,000, divide by 0.7.

cistern, etc., the closed bottle should be wholly immersed in the water, and the stopper then withdrawn. Before the bottle is filled, it should be rinsed out several times with the water. The bottle is then completely filled, a little water is poured away, and the clean stopper—which should also be rinsed with the water—is firmly inserted. It is sometimes advisable to secure the stopper in its place by tying over it a piece of clean linen cloth. The bottles containing the samples should be labelled with a distinctive number or letter, and a note made of the exact place where each sample was taken, with the hour and date of collection.

An analysis of a single sample affords information regarding the state of the water only at the time the sample was taken, and, as many waters vary in character from time to time, it is often necessary to make a periodic examination. After heavy rain, for example, some waters are often turbid; and pollution is frequently intermittent. An endeavour should be made to obtain samples, not only when the water is in its normal state, but also when its condition is abnormal.

The examination of the water should be commenced as soon as possible after the sample is collected.

PHYSICAL EXAMINATION.

The physical examination includes the colour, turbidity, odour, and taste of the water, and the determination of its electrical conductivity.

Odour.—When the bottle is first opened, ascertain whether the water has any odour. If it has little or none, warm 100 c.c. to about 50° in a clean flask, shake briskly, and try again. Good water has no smell, even when warmed.

Turbidity.—Examine the water contained in a large flask or bottle of colourless glass, and note its general appearance, *i.e.* whether it is bright and perfectly clear, or whether it is opalescent or turbid. If the turbidity is very pronounced, it may be desirable to ascertain approximately the amount of suspended matter.

Filter a measured volume (100 c.c. to 1000 c.c. according to the degree of turbidity) through a tared Gooch crucible

containing a *thick* pad of asbestos. Dry the crucible and contents in the steam-oven, cool, and weigh. Express the results in parts per 100,000.

Taste.—It is inadvisable to taste water samples indiscriminately, and, in any case, taste and smell are often difficult to differentiate. The presence of iron, salt, peat, etc., may confer on water a characteristic taste, but the presence of these substances can be ascertained in other ways. Pure water, properly aerated, may be described as tasteless.

Colour.—Special instruments are often used to measure the colour of water, but for most purposes it is sufficient to note the colour (and turbidity) of the water, contained in a 100 c.c. Nessler tube, as compared with a similar column of distilled water.

Distilled water is practically colourless when examined in this way. The presence of organic matter may confer a pale yellow tint. Moorland water containing peaty substances is often decidedly yellow or even reddish-brown.

Conductivity.—The conductivity of ideally pure water, expressed in gemmhos,¹ is about 0.04 at 18°, whereas that of ordinary distilled water is from twenty-five to one hundred times greater, say about 3 gemmhos. Natural waters have a much higher conductivity than distilled water, on account of the saline substances dissolved in them. The conductivity of natural waters varies from about 30 for a soft water like that of Loch Katrine, to 1000 or more for very hard or alkaline waters common in England, and to about 50,000 for sea water. If a water contains but a small quantity of sodium salts, the conductivity is approximately proportional to the “hardness” of the water, and every 20 units of conductivity at (20°) correspond, very roughly, to one “degree” of hardness (p. 350). For example, a sample of water was found to have a conductivity (at 20°) of 540, which indicates a hardness of from 25° to 30°. The hardness was found to be actually 27°.

A convenient, portable apparatus for conductivity measurements of this kind is the “Dionic Water Tester.” The apparatus consists of a glass cell fitted with platinum

¹ 1 gemmho = 1.0×10^{-6} reciprocal ohm.

electrodes, and a small continuous-current dynamo which is connected with the electrodes and with a direct-reading conductivity meter. The dynamo is turned by hand, and the conductivity of the water in the cell is registered on a dial provided. The only correction is for temperature, and the measurement occupies but a few moments.

The determination of conductivity is a most convenient and rapid method of *periodically* testing one and the same water supply. Any abnormal variation in the amount of dissolved salts—which can only be due to an influx of water of a different character and, it may be, from an objectionable source—is at once readily detected.

CHEMICAL EXAMINATION.

The chemical examination includes the determination of, more especially, the dissolved solids, ammonia, organic matter, chloride, nitrite, nitrate, “hardness,” acidity or alkalinity, and the action of the water on metals—especially lead. For some purposes, an accurate analysis of the saline constituents may also be required.

Total Solids.

(Residue on Evaporation.)

The residue obtained by evaporating a sample of water to dryness consists of all the non-volatile inorganic and organic substances that were dissolved or suspended in the water. If the water is very turbid, it is usually desirable to determine the solid matter in suspension, as described on p. 338. The filtered water is then used for the determination of the dissolved solids.

The quantity of water that should be evaporated depends on the probable amount of the saline constituents, and from 100 c.c. to 500 c.c. is usually sufficient. If the sample contains 10 parts of dissolved solids in 100,000, the residue from 250 c.c. weighs 0.025 gram.

Procedure.—Place a clean platinum basin in an air-oven at 180° for several minutes, then cool in a desiccator for ten minutes and weigh.

Measure the water in a graduated flask, transfer about

50 c.c. to the basin and evaporate on the steam-bath. Add more of the water at intervals, and finally rinse the flask with a little distilled water and add this to the basin.

After complete evaporation, remove the basin, wipe the outside carefully, and place it in an air-oven at 180° for an hour. Cool in a desiccator for ten minutes, and weigh. The residue is often hygroscopic. Replace the basin, therefore, in the air-oven for fifteen minutes, and weigh again as rapidly as possible. Repeat until constant weight is attained.

The results are not comparable unless the residue is always dried at the same temperature. Dried at 100° , the residual salts retain much combined water (water of crystallisation). Calcium sulphate retains half a molecule at 107° , and magnesium sulphate and calcium chloride 1 molecule even at 180° .

After weighing, heat the dish gently over a Bunsen flame, in order to obtain an idea of the amount of organic matter present in the residue. Observe whether the residue changes colour (becoming yellow, brown, or black). A smell of singed horn indicates the presence of *nitrogenous* organic matter. It may be noted, however, that if the residue contains much nitrate, very little charring will occur although organic matter is present.

The residue may be used to test for phosphate, as described on p. 349.

“Free” Ammonia and “Albumenoid” Ammonia.

Ammonia is often present in natural water, in the form of ammonium salts, and is usually referred to as “free” or “saline” ammonia. By distilling the water with a little sodium carbonate, the ammonia is found in the first portion of the distillate.

The so-called “albumenoid” ammonia is obtained by distilling the water with alkaline potassium permanganate solution after the removal of the “free” ammonia. The organic matter present in the water is decomposed by this treatment, but, as only a portion of the total organic nitrogen is thereby converted into ammonia, the results afford only an approximate measure of the nitrogenous organic substances present in the water.

The ammonia obtained in the distillates is determined colorimetrically by means of Nessler solution.

The following materials are required :—

(1) *Nessler Solution*; (2) *Standard Ammonium Chloride Solution*; and (3) *Ammonia-free Water*. These are prepared as described on p. 197.

(4) *Alkaline Potassium Permanganate Solution*.—Dissolve 4 grams of potassium permanganate in 750 c.c. of water, add 100 grams of sodium hydroxide, and boil the solution in a flask until the volume is reduced to about 500 c.c. After the solution has become cold, transfer it to a stoppered bottle.

(5) *Ignited Sodium Carbonate*.—Heat some sodium carbonate crystals in a platinum crucible to dull redness for about half an hour, then allow to cool, and transfer to a stoppered bottle.

The Apparatus, Fig. 83, consists of a distilling flask of not less than 1 litre capacity, and a condenser. The distilling flask, if not fitted with a ground-in stopper, is closed with a tube on which a bulb is blown and which contains lead shot in order to give it more weight; a piece of clean sheet

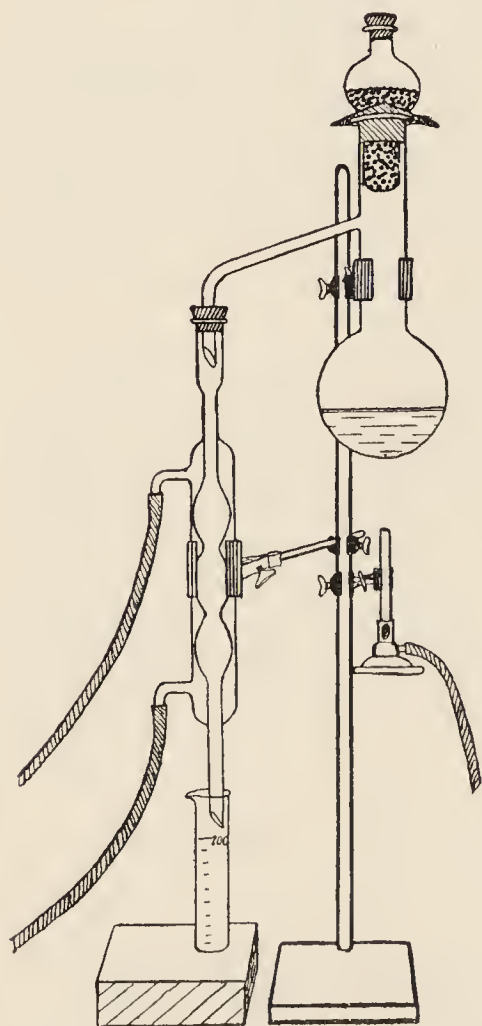


FIG. 83.

rubber, in which a small hole is cut with a cork borer, is drawn over this tube below the bulb, and the bulb rests on and closes the mouth of the flask. The side-tube of the distilling flask should pass well down into the inner tube of the condenser, and, if the tubes fit closely, no connecting cork need be used. If a rubber cork is used, it should be soaked in sodium hydroxide solution, and then thoroughly washed.

The determination of ammonia must be conducted in a room that contains no ammonia or ammonium salts, and the apparatus must not be used for any other purpose.

Preliminary Examination of the Water.—Measure 50 c.c. of the sample into a Nessler tube, add 2 c.c. of Nessler solution, and mix. From a burette, run 0.5 c.c. of the standard ammonium chloride solution into another tube, fill to the mark with ammonia-free water, add 2 c.c. of Nessler solution, and mix. If the colorations are of about equal intensity, use 500 c.c. of the water for the determination. As a rule, half a litre of a potable water is a suitable quantity. If less than half a litre is taken, dilute the measured quantity to 500 c.c. with ammonia-free water.

Determination of "Free" Ammonia.—Rinse the flask and condenser with hydrochloric acid, and then wash thoroughly with water. Place about 200 c.c. of distilled water and about 1 gram of recently ignited sodium carbonate in the flask, and distil fairly rapidly with a free flame. Allow the steam to blow through the condenser for several minutes, then admit the condensing water, and collect the distillate in Nessler tubes. Continue the distillation until the distillate gives no coloration with Nessler solution.

When the apparatus has been proved in this way to be ammonia-free, remove the flame and introduce, through a long-stemmed funnel, 500 c.c. of the water (or other suitable quantity, as determined by the preliminary examination), and proceed with the distillation. Distil fairly rapidly and as regularly as possible, and collect the distillate in three portions of 50 c.c. each, using Nessler tubes as receivers. Then interrupt the distillation and allow the apparatus to remain for the determination of the "albumenoid" ammonia in the residue. The whole of the ammonia in the portion of water taken is now contained in the distillate, and is determined colorimetrically as described on p. 198.

Determine the ammonia in the *second* portion of the distillate before the first portion is examined, in case the first portion contains too much ammonia (more than 0.1 mgrm.) for accurate comparison. If the second portion requires not more than 2 c.c. of the standard ammonium chloride solution to give a colour of equal intensity, the *whole* of the first portion should be examined in the same way. If the second portion requires more than 2 c.c., take one-half of the first portion (after mixing it well) and dilute to 50 c.c. with

ammonia-free water before adding the Nessler solution; the total ammonia in the first portion is then twice the observed quantity. Then test the third portion; it will probably contain very little or no ammonia.

From the total volume of the standard ammonium chloride solution required for the whole of the distillate, calculate the weight of ammonia in 100,000 parts of the water. One c.c. of the standard solution corresponds to 0.01 mgrm. of NH_3 , and if 4 c.c. in all were required, and 500 c.c. of water used, the water contained 0.008 part of "free" ammonia in 100,000.

Determination of "Albumenoid" Ammonia.—Add to the contents of the distillation flask 50 c.c. (one-tenth of the volume of water used) of the alkaline permanganate solution, and continue the distillation until four portions of 50 c.c. have been collected. Test each portion of the distillate, beginning with the last one.

Calculate the amount of "albumenoid" ammonia that 100,000 parts of the water would yield.

Reducing Power.

(Organic Matter.)

The organic matter in natural waters is mainly of plant or animal origin, and consists essentially of the decomposition products of decayed vegetation and of substances derived from the animal organism. Many of these organic substances—more particularly those derived from animal sources—contain nitrogen, and one of the simplest methods of obtaining information regarding the amount of organic matter in natural waters is the determination of the "albumenoid" ammonia, already described.

The organic matter is more or less easily oxidised, and an approximate estimate of the organic impurities in a water may also be arrived at by determining its reducing power, or its power of "absorbing" oxygen. The reducing power of a water is usually ascertained by measuring its action on a dilute, acid solution of potassium permanganate. The following solutions are required:—

(1) *Potassium Permanganate Solution (N/80).*—Dissolve 0.395 gram of the pure salt in cold water, and dilute the

solution to 1 litre. (One c.c. corresponds to 0.1 mgrm. of available oxygen.)

(2) *Dilute Sulphuric Acid*.—Pour 100 c.c. of pure concentrated sulphuric acid into 300 c.c. of water, cool the mixture partially, and add dilute potassium permanganate solution, drop by drop, until the acid acquires a permanent pink tinge.

(3) *Sodium Thiosulphate Solution* (N/250).—Dissolve 1 gram of the pure salt in 1 litre of water.

(4) *Potassium Iodide Solution*.—Dissolve 10 grams in 100 c.c. of water.

Procedure.—Measure 250 c.c. of the water to be examined into a perfectly clean, stoppered bottle (500 c.c.). Place the bottle in a thermostat or air-bath at 27°, and, when the temperature of the water has become constant, add 10 c.c. of the dilute sulphuric acid and 10 c.c. of the potassium permanganate solution. Allow the bottle to remain in the bath for four hours.¹ Examine it from time to time, and if a marked diminution in the depth of the pink colour is observed, add another 10 c.c. of the permanganate solution.

Meanwhile standardise the sodium thiosulphate solution as follows:—Place 250 c.c. of freshly distilled water in a 500 c.c. bottle, add 10 c.c. of the sulphuric acid, 10 c.c. of the permanganate solution, and then 1 c.c. of the potassium iodide solution. Titrate the liberated iodine with the thiosulphate, starch solution being used as indicator as usual. The volume of thiosulphate solution required corresponds to 1 mgrm. of available oxygen.

After the lapse of four hours, remove the bottle containing the water sample and cool the contents by immersing the bottle in water. Add 1 c.c. of the potassium iodide solution, and titrate with the thiosulphate.

If 30 c.c. of the thiosulphate correspond to 1 mgrm. of oxygen, and if 24 c.c. were required after digesting the water with the permanganate, the amount of oxygen absorbed by 250 c.c. of the water is $\frac{30-24}{30}=0.2$ mgrm., *i.e.* 0.08 part per 100,000.

¹ Widely varying temperatures and periods of digestion are employed, and the results are not comparable unless obtained by identical methods.

Chloride.

All natural water contains chloride. Rain water may contain only a mere trace, and river water less than 1 part of "chlorine" in 100,000, but a much larger quantity is often present, especially in well water.

The following solutions are required:—(1) A solution of silver nitrate containing 4.79 grams per litre. One c.c. of this solution corresponds to 1 mgrm. of chlorine. (2) A 2 per cent. solution of potassium chromate, free from chloride (see footnote on p. 122).

Procedure.—Measure 100 c.c. of the water into a porcelain basin, add 1 c.c. of the potassium chromate solution, and run in the silver nitrate solution from a burette, while stirring briskly, until a faint, permanent reddish-brown tinge is obtained. Usually, too much silver nitrate is added in the first titration. Add, therefore, a few drops of ammonium chloride in order to destroy the reddish tinge, and use this mixture, which has a pure yellow colour, as a guide for a second titration made in another similar basin. On account of the solubility of silver chromate, a slight excess—about 0.2 c.c.—of silver nitrate must be added before the reddish tinge (precipitated silver chromate) is apparent. The number of cubic centimetres of silver nitrate solution used, less 0.2 c.c., gives the milligrams of chloride (Cl) in 100 c.c. of the water, *i.e.* parts per 100,000.

Alternative Procedure.—To 100 c.c. of the water, add 1 c.c. of the potassium chromate solution. Run in the silver nitrate solution until, after stirring, a permanent reddish tinge is obtained. Then add, from a measuring cylinder, more of the water sample until the reddish tinge is just destroyed. (From 5 to 20 c.c. may be required.) The volume of silver nitrate solution used corresponds to the chloride in 100 c.c. of the water plus *one-half* of the further quantity of water added. Calculate the number of cubic centimetres of silver nitrate solution required for 100 c.c. of the water.

Notes.—If the water contains less than 1 part of chloride in 100,000, use a larger volume and evaporate on the steam-bath to about 100 c.c., then cool, and titrate.

If the water is acid, add sodium bicarbonate (sufficient to render the water faintly alkaline) before titrating.

If the water is peaty and highly coloured, or if it is sewage-polluted and contains hydrogen sulphide, add a small quantity of lime-water (free from chloride) to the measured portion of the water; pass a current of carbon dioxide through the liquid, then boil for a few minutes, cool, and filter. Determine the chloride in the filtrate as directed.

Nitrite.

Nitrite is rarely found in natural waters, except in minute traces, and a qualitative test is usually all that is necessary. The following solutions are required:—

(1) *Griess-Llosvay Reagent*.—Dissolve (a) 0.1 gram of α -naphthylamine by warming with about 50 c.c. of water mixed with 10 c.c. of glacial acetic acid, (b) 0.5 gram of sulphanilic acid in the same quantities of hot water and acetic acid. Mix the solutions (a) and (b), and dilute to 300 c.c. If the solution becomes coloured by keeping, shake with a little zinc dust, and filter.

(2) *Standard Sodium Nitrite Solution*.—Dissolve 0.335 gram of pure silver nitrite in hot water, add excess of sodium chloride (about 0.2 gram), cool, and dilute to 1 litre. (Keep this solution in the dark.) For immediate use, dilute 5 c.c. of the clear liquid to 1 litre. This solution contains 0.05 part of nitrite (NO_2) in 100,000.

Detection of Nitrite.—To 50 c.c. of the water sample, add 2 c.c. of the reagent, and warm to about 80° . If nitrite is present, a pink coloration is obtained. With as little as 0.01 part of nitrite (NO_2) in 100,000, the colour appears almost immediately, and much smaller amounts give a decided reaction within a few minutes.

Quantitative Determination.—Place 50 c.c. of the water sample and of the standard nitrite solution in two Nessler tubes, and add 2 c.c. of the reagent to each. Cover the tubes (in order to protect the contents from any trace of nitrite in the air), and set them aside for twenty minutes. If, on then comparing the tubes, the water sample is found to give a darker coloration than the standard, use a smaller

quantity of the sample and dilute with water (free from nitrite) to 50 c.c.; if the water sample contains less nitrite than the standard, dilute the latter; and, in either case repeat the experiment until the tints in the two Nessler tubes match one another.

The amount of nitrite (NO_2) in the water can then be calculated.

Nitrate.

Practically all natural waters contain at least a trace of nitrate. Nitrate, like chloride, is itself innocuous, but, from a hygienic standpoint, the presence of a large amount of nitrate in a drinking water is by no means unimportant.

Detection of Nitrate.—In a test-tube, mix 1 c.c. of the water, drop by drop, with 3 c.c. of concentrated sulphuric acid, cool, and then add a few milligrams of brucine.

If nitrate is present, a red coloration is obtained. With 10 parts of nitrate (NO_3) in 100,000, the colour is cherry-red, changing to orange; with 1 part, it is rose-red; and with 0.1 part, a pale rose-coloured solution is obtained.

In case the sulphuric acid contains a trace of nitrate, it is essential to make a parallel experiment with distilled water, and, if nitrate is present, to compare the coloration with that given by the water sample. Nitrite gives no coloration with brucine and sulphuric acid, provided the above directions are exactly followed. Ferrous salts interfere and, if present, must therefore be removed by means of sodium hydroxide free from nitrate.

Quantitative Determination.—The nitrate is reduced to an ammonium salt by means of a copper-zinc couple, and the ammonia is then determined by means of Nessler solution. From 10 c.c. to 100 c.c. of the water, according to the amount of nitrate present, is required for the determination. If about 1 part of nitrate (NO_3) in 100,000 is probably present, use 50 c.c.

Preparation of the Copper-Zinc Couple.—Roll a piece of zinc foil, 3 inches square, into a cylinder about $\frac{3}{4}$ inch diameter. Dip the foil into hydrochloric acid in order to clean it, and then wash it with water. Place it in a large

test-tube, and cover it with a 3 per cent. solution of copper sulphate for a few minutes until it is completely coated with a black deposit of copper. Pour away the copper sulphate solution, and wash the foil with distilled water without removing it from the test-tube.

Reduction of the Nitrate.—If the water contains much ammonia, dilute the measured portion (if necessary) to about 100 c.c., and boil it until the volume is reduced to about 50 c.c. Cool the water, transfer it to the test-tube containing the copper-zinc couple, and add dilute hydrochloric acid (3 to 4 drops) sufficient to cause, after several minutes, a slight evolution of hydrogen. Cover the test-tube with a watch-glass, and set aside overnight.

The reduction is more rapid at higher temperatures, and at 50° it is complete in an hour.

Determination of the Ammonia.—Place about 400 c.c. of distilled water and about 1 gram of ignited sodium carbonate in an apparatus similar to that used for the determination of ammonia in water, and remove any ammonia in the apparatus by distilling over about 100 c.c. Transfer the solution containing the reduced nitrate to the distilling flask, add the washings of the copper-zinc couple, and distil. Collect the distillate in two portions of 50 c.c., and determine the ammonia in each portion colorimetrically as described on p. 198.

From the amount of ammonia thus found, calculate the corresponding amount of nitrate (NO_3). Any nitrite in the water is of course included, but the amount is usually too small to affect the result appreciably.

Phosphate.

Phosphate is rarely present in natural waters, except in traces. As a rule, only a qualitative test need be made.

Dissolve the residue obtained in the determination of the "Total Solids" (p. 340) in dilute nitric acid, transfer the solution to a porcelain basin, and evaporate to dryness on the steam-bath. Moisten the residue with nitric acid, and again evaporate to complete dryness. Then add a few drops of nitric acid and 5 c.c. of water, warm, and filter. Add 5 c.c.

of ammonium molybdate solution, warm to about 60° , and set aside. If phosphate is present, a yellow turbidity, or a distinct precipitate, is obtained, and its amount may be approximately estimated by comparing it with known amounts of ammonium phospho-molybdate.

Hardness.

Natural waters are familiarly described as "hard" or "soft," these terms having reference to the action of the water on soap. A water is said to be "soft" if it gives an immediate lather with soap, and "hard" if a lather is obtained with difficulty. The "hardness" of a water thus refers to its soap-destroying power, and is due almost entirely to the calcium and magnesium salts dissolved in the water.

Hardness is expressed in degrees, 1° corresponding to 1 part of calcium carbonate, or its equivalent in other calcium and magnesium salts, in 100,000 parts of water.

It is usual to distinguish between "temporary" and "permanent" hardness. The former is due to the presence of calcium and magnesium bicarbonates, and the latter mainly to the corresponding sulphates and chlorides.

Temporary Hardness is, strictly speaking, the hardness that disappears on boiling the water. The bicarbonates are thereby decomposed and normal carbonates are precipitated; but, as the solubility of normal calcium carbonate in boiling water amounts to about 2 parts in 100,000, and as magnesium carbonate is still more soluble, no diminution in hardness will occur on boiling unless the original hardness, due to bicarbonate, exceeds at least 2° .

Permanent Hardness, *i.e.* the hardness that remains after boiling the water, is due not only to the sulphates and chlorides of calcium and magnesium, but also to the calcium and magnesium carbonates that still remain dissolved.

The hardness of a water, or its soap-destroying power, may be determined by means of a standardised solution of soap. The soap solution is gradually added to a measured volume of the water until, after vigorous agitation, a permanent lather is obtained. The hardness determined in

this way corresponds *approximately* to the amount of calcium and magnesium salts dissolved in the water. When it is necessary to ascertain the respective amounts of these salts accurately, the calcium and magnesium must be determined gravimetrically as described on p. 361, but for many practical purposes sufficient information is obtained more expeditiously by the volumetric methods described below.

Determination of Temporary Hardness or "Alkalinity."—The bicarbonates of calcium and magnesium are, as a rule, the only substances in a natural water which, on account of hydrolysis, confer alkalinity (as shown by certain indicators) on the water, and the bicarbonate hardness is sometimes referred to as the "alkalinity" of the water. The "alkalinity" is determined as follows:—

Measure 100 c.c. of the water into a casserole. Add 2 c.c. of methyl red, and run in 0.02N hydrochloric acid until the liquid becomes light red. Boil for about a minute; if too much acid has not been added, the yellow colour of the indicator will reappear. Add more acid, drop by drop, until the first sign of a red tinge, which is not destroyed by further boiling, is obtained. A more convenient and expeditious method of procedure is to add excess of acid (about 1 c.c. in excess) and then, after boiling for about a minute, to titrate back with 0.02N baryta solution. The end-point of the titration is sharply defined.

One c.c. of 0.02N acid corresponds to 0.001 gram of CaCO_3 ; and, since 100 c.c. of the water was taken, each cubic centimetre of the standard acid used in the titration represents 1 part of calcium carbonate in 100,000 parts of water, or 1° of hardness.

Some natural waters contain sodium carbonate, and in that case a correction, referred to on p. 352, must be applied to the "alkalinity" before it is taken as a measure of the bicarbonate hardness.

Determination of Permanent Hardness.—Measure 100 c.c. of the water into a platinum basin, add 10 c.c.¹ of approximately 0.04N potassium carbonate, and evaporate

¹ If the permanent hardness is believed to exceed 15°, more than 10 c.c. of the potassium carbonate must be added.

to dryness on the steam-bath.¹ Extract the residue as follows:—Pour into the basin 10 c.c. of hot, 20 per cent. alcohol (20 c.c. of pure, absolute alcohol—not rectified spirit—diluted to 100 c.c.). Bring the hot liquid into contact with every portion of the residue, warm on the steam-bath for about a minute, and filter through a $5\frac{1}{2}$ -cm. paper into a casserole. (Filtration is slow unless a funnel with a looped suction-tube is used.) Carefully rinse the basin four times with cold, 90 per cent. alcohol (use about 5 c.c. each time, from a wash-bottle), and pour through the filter. Then wash the filter six times with the same alcohol. (The platinum basin and the filter, containing the precipitated carbonates of calcium and magnesium, are set aside for the determination of total hardness to be described below.)

Titrate the filtrate with 0.02N hydrochloric acid, using methyl red as indicator, as described under temporary hardness. In the same manner, titrate 10 c.c. of the original potassium carbonate solution, previously diluted with 90 per cent. alcohol to 50 c.c.

The permanent hardness, in degrees, is equal to the amount of potassium carbonate, measured in cubic centimetres of the 0.02N acid, required to precipitate the calcium and magnesium sulphates and chlorides in 100 c.c. of the water. If, for example, 10 c.c. of the potassium carbonate solution required 20.45 c.c. of 0.02N acid, and the residual potassium carbonate in the filtrate required 16.30 c.c., the permanent hardness is equal to $20.45 - 16.30 = 4.15^\circ$.

If the original water contains sodium carbonate, there can be no permanent hardness, and, in the foregoing determination, the filtrate will require *more* acid than that necessary to neutralise the potassium carbonate added to the water. The excess represents the amount of sodium carbonate originally present in the water, and it must be deducted from the “alkalinity” in order to find the bicarbonate hardness.

Determination of Total Hardness.—The sum of the temporary and the permanent hardness gives the total

¹ The evaporation must be conducted in such a manner as to avoid contamination of the contents of the basin with oxides of sulphur from a coal-gas flame. A steam-bath with an external source of steam and provided with a cover (Fig. 12, p. 24) is a satisfactory arrangement.

hardness of the water. If 100 c.c. of the water be first neutralised (as in determining temporary hardness) and then evaporated with a known quantity of potassium carbonate, the amount of the latter required to precipitate the calcium and magnesium salts is equivalent in that case to the total hardness instead of the permanent hardness. The total hardness may also be determined directly as follows:—

Measure 5 c.c.¹ of 0.1N hydrochloric acid into the basin in which the evaporation described under permanent hardness was conducted. Place the basin on a perforated silica plate (p. 144), warm with a small flame until the acid just boils, and bring the acid into contact with the whole interior of the basin. Warm the acid again and pour it through the filter, care being taken that the acid comes into contact with every part of the paper, and receive the filtrate in a casserole. Rinse the basin and wash the filter thoroughly with cold water. Boil the filtrate for a minute on a silica plate, add 1 c.c. of methyl red, and titrate with 0.02N baryta solution.

The total hardness of the water, in degrees, is equal to the number of cubic centimetres of 0.02N acid required to decompose the carbonates obtained from 100 c.c. of the water.

Determination of Calcium and Magnesium.—The water is evaporated with ammonium carbonate. The dry residue, containing the calcium and magnesium as carbonates, is extracted with hot ammonium carbonate solution which dissolves the magnesium carbonate, but is practically without action on the calcium carbonate. The amount of the latter is ascertained and gives the hardness due to calcium salts. The difference between the total hardness and that due to calcium salts gives the hardness due to magnesium salts.

Measure 100 c.c. of the water into a platinum basin, add 10 c.c. of a 2 per cent. solution of ammonium carbonate (2 grams of the solid and 1 c.c. of concentrated ammonia in 100 c.c.), and evaporate to dryness on the steam-bath. Pour 15 c.c. of the same ammonium carbonate solution into the basin, bring the liquid into contact with the whole of the

¹ In order to ensure complete solution of the carbonates, at least twice the equivalent amount of 0.1 N acid must be used. Five c.c. is sufficient if the total hardness is less than 10°.

residue, and allow the basin to remain on the steam-bath for about two minutes. Filter through a $5\frac{1}{2}$ -cm. paper, retaining the undissolved carbonate as far as possible in the basin. Repeat the extraction twice, using about 10 c.c. of ammonium carbonate each time.

Rinse the platinum basin four times with 90 per cent. alcohol, and wash the filter with the same alcohol until the filtrate is free from alkali. (Absence of alkali may be ascertained by allowing about 5 c.c. of the filtrate to drop into a little water containing methyl red and a trace of 0.02N acid.) Dissolve the calcium carbonate, which now alone remains in the basin and on the filter, in a measured volume of 0.1N hydrochloric acid (usually 5 c.c. to 10 c.c.¹), and titrate the excess of acid with 0.02N baryta solution, as described under total hardness.

The amount of calcium in the water, expressed in degrees of hardness, is then calculated. If the hardness due to calcium is found to be 6° and the total hardness was 10°, the hardness due to magnesium corresponds to 4°. As degrees of hardness are expressed in terms of calcium carbonate, it is a simple matter to convert the results into milligrams of calcium and magnesium per litre, or any other more convenient units.

Alternative Method.—In this method, which may be found preferable for very hard waters, the calcium is precipitated as oxalate and is determined by titration with standard potassium permanganate solution.

Measure 100 c.c. of the water into a glass basin, add 1 c.c. of dilute hydrochloric acid, and heat until almost boiling. To the hot solution, add ammonia until it is ammoniacal and then 3 c.c. of a freshly prepared saturated solution of ammonium oxalate. Evaporate on the steam-bath until the volume of the liquid is about 10 c.c. Add 10 c.c. of ammonia, filter the calcium oxalate through a small paper, and wash with warm water containing a little ammonia until the filtrate is free from chloride. Pierce the apex of the filter paper with a pointed glass rod, and wash the precipitate into a small conical flask. Heat 5 c.c. of dilute sulphuric acid in the original glass basin (in case any of the precipitate remains in it), and pour the hot acid into the filter, care

¹ See footnote on p. 353.

being taken that the acid comes into contact with every part of the paper. Rinse the basin and wash the filter with hot water. Titrate the hot solution with 0.02N potassium permanganate.

The permanganate solution should be standardised by means of a dilute solution of calcium chloride of known concentration (prepared from calcite) under conditions similar to those described above.

Relative Acidity and Alkalinity.

Ideally pure water is neutral, but natural waters may be neutral, acid, or alkaline, according to the substances dissolved in them. The acidity or alkalinity of water is usually determined by means of an indicator, such as litmus or phenolphthalein, but since different indicators give different results, one and the same water may appear acid when tested with one indicator, and alkaline with another. Ordinary distilled water, for example, appears acid with litmus or phenolphthalein, and approximately neutral with methyl orange.

The so-called "alkalinity" of a water, as determined by titration (compare temporary hardness), is really a measure of the *potential* alkalinity of the water, and not of its *actual* alkalinity. The potential alkalinity of a solution of sodium bicarbonate, for example, as determined by titration with methyl orange as indicator, is the same as that of a solution of sodium hydroxide of the same molecular concentration; whereas sodium bicarbonate solution appears neutral, and sodium hydroxide solution alkaline, when tested with phenolphthalein. The actual alkalinities of these solutions are, in fact, very different, and it is on the actual acidity (or alkalinity) that many of the properties of a solution, such as the rate of its action on metals, depend.

Ideally pure water and all neutral solutions contain the acid ion (hydrion) H^+ , and the alkaline ion (hydroxidion) OH^- , in chemically equivalent proportions; and the product of the concentrations of these ions in all dilute aqueous solutions as well as in pure water is constant.¹ If an excess of either

¹ The exact values depend on temperature. At 18°, the concentrations of hydrion and hydroxidion in pure water are each $0.85 \times 10^{-7} = 10^{-7.07}$ normal, and at the same temperature the product of the concentrations of these ions in water and in any dilute aqueous solution is therefore $0.72 \times 10^{-14} = 10^{-14.14}$.

ion is present, as is usually the case in ordinary water, the water is either acid or alkaline, and the acidity or alkalinity may be stated in terms of the hydrion concentration.

It is more convenient, for practical purposes, to express the acidity or alkalinity of ordinary water in terms of the acidity or alkalinity of ideally pure water at the same temperature. If the acidity of pure water is taken as 1, then the alkalinity is also 1; and if the hydrion concentration in a sample of ordinary water is twice the hydrion concentration in pure water at the same temperature, it would be stated to have a *relative acidity* of 2. (Its *relative alkalinity* would be half that of pure water, viz., 0.5.)

The following method of determining the relative acidity or alkalinity of a water is a colorimetric one, and is based on the use of standard solutions of definite acidity and alkalinity in which azolitmin assumes a red tint when the solution is decidedly acid, passes through intermediate shades of purple, and becomes finally blue when the solution is decidedly alkaline. The following solutions are required:—

(1) *Disodium Phosphate*.—Dissolve 23.88 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in water, and dilute the solution to 1 litre. “Chemically pure” crystals, free from efflorescence, are satisfactory. This solution is alkaline.

(2) *Potassium Dihydrogen Phosphate*.—Dissolve 9.08 grams of KH_2PO_4 in water, and dilute the solution to 1 litre. The salt must be free from chloride and sulphate. This solution is acid.

(3) *A Neutral Solution*.—Mix 250 c.c. of the disodium phosphate solution with 158 c.c. of the potassium dihydrogen phosphate solution. The solutions may be measured with sufficient accuracy in a narrow graduated cylinder.

(4) *Azolitmin*.—Dissolve 0.1 gram of azolitmin in 100 c.c. of water.

Two methods of procedure are described below. The first method is suitable for waters that are practically free from colour, and the second method is used for coloured waters. If the water is turbid, the suspended matter must be allowed to subside and a clear portion siphoned off. Filtration must be avoided, since contact with filter paper almost invariably increases the acidity of the water.

Procedure in the Case of a Colourless Water.—Measure 25 c.c. of the water and of the neutral standard into two porcelain basins of about 120 c.c. capacity, add 1 c.c. of azolitmin solution to each, and compare the tints.

(a) If the water is decidedly acid, measure 25 c.c. of the *acid* phosphate into another similar basin, add the indicator, and run in the alkaline phosphate from a burette until the colour of the mixture matches that of the water sample with indicator. The volume of the water sample should be kept roughly equal to the volume of the mixed phosphates by adding more of the sample at intervals. Then perform a second experiment in the same manner, commencing, however, with a volume of the water sample such that, when a good match is obtained, the bulk of the liquids in the two basins is practically the same. In this way, the concentration of the indicator is kept the same, and the exact matching of the tints is easier. The comparison should be made in good diffused daylight. The acidity of the water, according to the volume of alkaline phosphate required, is given in Table I.

TABLE I.

For decidedly acid waters.
Volume of KH_2PO_4 used = 25 c.c.

Volume of Na_2HPO_4 required.	Relative Acidity.	Concentration of H^+	Volume of Na_2HPO_4 required.	Relative Acidity.	Concentration of H^+
...	300	$10^{-4.5}$	8.1	4.5	$10^{-6.35}$
0.3	100	$10^{-5.0}$	9.2	4.0	$10^{-6.4}$
0.6	50	$10^{-5.3}$	10.5	3.5	$10^{-6.45}$
1.7	20	$10^{-5.7}$	12.3	3.0	$10^{-6.5}$
2.2	15	$10^{-5.8}$	15.2	2.5	$10^{-6.6}$
3.6	10	$10^{-6.0}$	19.2	2.0	$10^{-6.7}$
4.0	9	$10^{-6.05}$	21.4	1.8	$10^{-6.75}$
4.5	8	$10^{-6.1}$	24.2	1.6	$10^{-6.8}$
5.2	7	$10^{-6.15}$	27.7	1.4	$10^{-6.85}$
6.1	6	$10^{-6.2}$	32.7	1.2	$10^{-6.9}$
7.3	5	$10^{-6.3}$	39.4	1.0*	10^{-7*}

* These values correspond to neutrality; in a neutral solution the concentration of H^+ is 1×10^{-7} normal (but compare footnote on p. 355).

(b) If the water is alkaline or nearly neutral, measure 25 c.c. of the *alkaline* phosphate into a basin, add the indicator, and run in the acid phosphate until a good match

is obtained. The alkalinity or acidity of the sample, according to the volume of acid phosphate required, is given in Table II.

TABLE II.

For nearly neutral and alkaline waters.
Volume of Na₂HPO₄ used = 25 c.c.

Volume of KH ₂ PO ₄ required.	Relative Alkalinity.	Concentration of H ⁺	Volume of KH ₂ PO ₄ required.	Relative Alkalinity.	Relative Acidity.	Concentration of H ⁺
...	150	10 ^{-9.2}	4.5	3.0	...	10 ^{-7.5}
0.25	50	10 ^{-8.7}	5.6	2.5	...	10 ^{-7.4}
0.75	18	10 ^{-8.25}	7.2	2.0	...	10 ^{-7.3}
0.9	16	10 ^{-8.2}	8.2	1.8	...	10 ^{-7.25}
1.1	13	10 ^{-8.1}	9.3	1.6	...	10 ^{-7.2}
1.4	10	10 ^{-8.0}	10.8	1.4	...	10 ^{-7.15}
1.8	8.5	10 ^{-7.9}	12.9	1.2	...	10 ^{-7.1}
2.35	6.5	10 ^{-7.8}	15.8	1.0*	1.0	10 ^{-7.0}
2.7	5.5	10 ^{-7.75}	19.1	...	1.2	10 ^{-6.9}
3.15	5.0	10 ^{-7.7}	22.6	...	1.4	10 ^{-6.85}
3.7	4.0	10 ^{-7.6}	25.8	...	1.6	10 ^{-6.8}

* Neutral.

Procedure in the Case of a Coloured Water.—In this case, it is necessary to compensate for the colour of the

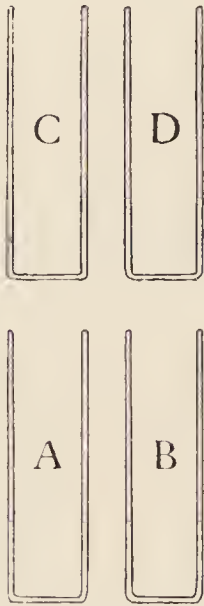


FIG. 84.

- A contains distilled water.
- B contains the water sample.
- C contains the water sample and indicator.
- D contains the phosphate standard and indicator.

water by matching the solutions in 50 c.c. Nessler tubes. The tubes are arranged as shown in Fig. 84. The light that illuminates the phosphate standard in D is made to pass also through the tube B containing the water sample (without indicator), whilst the light that reaches the eye through the water sample (with indicator) in C passes also through a column of distilled water in A.

Make a preliminary titration by the first method. Suppose, for example, that the water is acid and is found to match (approximately) a mixture of 25 c.c. of the acid phosphate with 15 c.c. of the alkaline phosphate (total volume of the mixture = 40 c.c.). Measure 40 c.c. of distilled water into the tube A, an equal volume of the water sample into

the tubes B and C, and 25 c.c. of the acid phosphate into the tube D. Add 1 c.c. of azolitmin to C and D, and run the alkaline phosphate into D (mixing the solutions by means of a glass tube on which a bulb of appropriate size is blown) until the tints in C and D match exactly. The tubes A and C are held in the left hand and B and D in the right, and the two pairs of tubes are looked into from above.

Notes.—Hard water—if the hardness is due mainly to bicarbonate—is alkaline, and soft water is often acid. If the acidity of a soft water containing bicarbonate is due entirely to carbonic acid, the water will become alkaline on passing a current of air, free from carbon dioxide, through the water. The acidity must be due to some acid other than carbonic acid if this treatment does not remove it. It should be noted, however, that a water from which the carbon dioxide has been entirely removed is no longer in equilibrium with normal air, and reabsorption of carbon dioxide commences *immediately* the water is exposed to ordinary air.

Lead.

From a hygienic standpoint, it is most important that a water supply should not dissolve more than a mere trace of lead from the service pipes. The action of a water on lead is closely connected with its *effective* acidity. Hard water, if the hardness is due to bicarbonate, is alkaline, and, as a rule, its only action is to coat the lead pipe with an insoluble film which adheres to the pipe, and practically no lead is found in the water. Soft water and moorland peaty water, which are often acid, not only tarnish lead but usually dissolve it, and the contamination may be such that the water is directly injurious to health. On the other hand, some very soft waters, such as the Glasgow water supply, are without appreciable solvent action on lead.

If a water supply is suspected of causing lead poisoning, samples should be taken after the water has been in contact with the service pipes for various lengths of time, up to twelve hours.

Detection of Lead.—To 100 c.c. of the water, add 2 c.c. of acetic acid and 2 c.c. of hydrogen sulphide solution. A

brown coloration is obtained if the water contains more than 0.01 part of lead in 100,000. Iron does not interfere with the test, but copper gives a similar coloration. Copper is rarely present, however, in drinking water.

A very much smaller quantity of lead can be detected in the following way :—

Filter about a litre of the water through a small plug of pure cotton wool placed in a funnel. Practically all the lead salt is retained by the cotton wool. Redissolve the lead by pouring hot, dilute acetic acid over the cotton wool, and then wash with distilled water. In this way the concentration of the lead may be increased almost a hundredfold. Test the solution with hydrogen sulphide.

Quantitative Determination.—If the hydrogen sulphide test shows the presence of lead, determine the amount colorimetrically as described on p. 198.

Action of Water on Lead.

The action of a water on lead may be determined as follows :—

Procure some new $\frac{1}{2}$ -inch lead service piping, and cut it into lengths of $2\frac{1}{2}$ feet. Close one end of each piece in a vice. The capacity of the tubes so formed is about 100 c.c.

Carefully rinse out two or three of the tubes with the water under examination, and then fill the tubes *completely* with the water. Fill other two or three tubes with tap water that is known to be satisfactory as regards its action on lead. Cork the tubes so that no air is enclosed, and set them aside for twenty-four hours. Then empty the contents of the tubes into 100 c.c. Nessler tubes, and determine the lead colorimetrically. Repeat the experiment until practically constant results are obtained.

When tested in this way, most waters will dissolve at least a trace of lead. The actual amount of lead found in the water taken from the tubes will probably be much more than would be present in a domestic water supply under ordinary circumstances, but with a really satisfactory water it should not be more than about 0.1 part of lead in 100,000. A comparison with the amount of lead dissolved in the tubes containing the tap water is a useful guide.

Iron.

Natural waters containing more than about 0.02 part of iron per 100,000 usually become opalescent or turbid on exposure to the air, owing to the decomposition and oxidation of the ferrous hydrogen carbonate. The precipitation of the iron as ferric hydroxide does not occur so readily in the case of a water containing peaty organic matter.

Quantitative Determination.—To 100 c.c. of the water, add 5 c.c. of concentrated hydrochloric acid and a few crystals of potassium chlorate, and evaporate to dryness. Dissolve the residue in 1 c.c. of concentrated hydrochloric acid, dilute to 100 c.c., and determine the iron colorimetrically by means of ammonium thiocyanate (p. 192).

DETERMINATION OF THE SALINE CONSTITUENTS.

An accurate analysis of the salts dissolved in a natural water is sometimes required, either for scientific or technical purposes. The analysis involves the determination of silica, iron, aluminium, manganese (rarely), calcium, magnesium, sodium, and potassium; and carbonate, sulphate, chloride, and nitrate.

Determination of Silica, Iron, Aluminium, Calcium, and Magnesium.

Measure from 1 to 2 litres of the water into a large silica flask, add 10 c.c. of concentrated hydrochloric acid, and boil down to about 100 c.c. A large Bunsen flame or a ring burner may be used at first, and the evaporation of a litre of water need not take longer than an hour and a half. Transfer the residual solution and the rinsings of the flask to a platinum basin, and evaporate to complete dryness on the steam-bath.

Determination of Silica.—Add 2 c.c. of concentrated hydrochloric acid to the dry residue and, after a few minutes, dilute with 10 c.c. of water. Warm the covered basin on the steam-bath for several minutes, then filter through a small paper, and wash the insoluble residue with warm water containing a little hydrochloric acid. Incinerate the paper and

ignite the insoluble residue in a platinum crucible, and weigh. The "silica" must be examined for impurities as described on p. 255. It may contain calcium sulphate.

Determination of Iron, Aluminium, Calcium, and Magnesium.—To the filtrate from the silica, contained in a porcelain (not platinum) basin, add a few drops of concentrated nitric acid, evaporate to dryness, and ignite gently in order to destroy organic matter. Moisten the residue with 2 c.c. of concentrated nitric acid, add 10 c.c. of hot water, filter, and wash with warm water containing a little nitric acid. Determine the iron, aluminium, calcium, and magnesium as described on pp. 282-284.

Determination of Sodium and Potassium.

Evaporate a measured volume of the water, in the manner already described, to about 100 c.c. Transfer to a platinum basin and concentrate to 50 c.c. To the hot solution, add a slight excess of a hot, saturated solution of barium hydroxide, in order to precipitate iron, magnesium, sulphate, etc. Evaporate until the volume of the liquid is about 25 c.c., then filter the precipitate and wash it with hot water. The filtrate contains barium, calcium, sodium, and potassium. Remove the calcium and barium, and determine the sodium and potassium, as described on pp. 290-291.

Determination of Sulphate, Carbonate, Chloride, and Nitrate.

Sulphate.—Determine whether much sulphate or only a small amount is present by adding one drop of dilute hydrochloric acid and a few drops of barium chloride solution to 10 c.c. of the water; 10 parts, or more, of sulphate (SO_4) in 100,000 give an immediate precipitate.

Take 200 c.c. of the water (or more if the precipitate with barium chloride is small and forms slowly), add about 2 c.c. of dilute hydrochloric acid, and evaporate to about 50 c.c.¹ Determine the sulphate as barium sulphate (p. 169).

Carbonate.—The total "alkalinity" of the water, as determined by titration with hydrochloric acid and described under "Hardness," gives the amount of carbonate present.

¹ See footnote on p. 352.

One c.c. of 0.02N acid corresponds to 0.6 mgrm. CO_3 , and if 100 c.c. of the water is titrated, each cubic centimetre of the acid required corresponds to 0.6 part of carbonate in 100,000.

Chloride and Nitrate.—The determination of chloride and of nitrate has been already described.

SIGNIFICANCE OF THE RESULTS OF ANALYSIS IN THE CASE OF A POTABLE WATER.

The purity of a drinking water is judged mainly from the amounts of nitrogenous substances (free and albumenoid ammonia, nitrite, and nitrate), organic matter (absorption of oxygen), and chloride that it contains. It is practically impossible to fix definite standards of purity based on the amounts of any of the above substances. A water must be judged on its own merits, and with full knowledge of the source from which it is derived. No attempt is here made to discuss the full significance of the results of analysis. A few notes are given below, and further information will be found in Thresh's *Examination of Waters and Water Supplies*.

Residue on Evaporation.—It is desirable that this should not exceed 50 parts per 100,000.

Hardness.—If the total hardness is under 5° , the water may be considered "soft"; from 5° to 10° , "fairly soft"; from 10° to 20° , "hard"; and over 20° , "very hard." If the hardness exceeds 30° , the water is very unsuitable for general purposes.

Chloride.—Sewage contains chloride, and the presence of much chloride in a water (especially if accompanied by an excessive amount of nitrate) may be an index of pollution—provided the chloride is not derived from sea water or other natural source. As a general rule, a surface water contains less than 2 parts of chloride (Cl) in 100,000. Well water may contain much more.

Free and Albumenoid Ammonia.—Decaying organic matter and sewage contain ammonia, and the presence of more than about 0.005 part of free ammonia in 100,000 is significant of possible pollution. If a water yields more free ammonia than albumenoid ammonia, the nitrogenous

impurity is probably derived from sewage. On the other hand, *slight* sewage pollution—sufficient to render a water unsafe—cannot always be detected by chemical methods. Peaty water yields the albumenoid ammonia slowly, and usually in larger amount than the free ammonia.

A satisfactory water seldom yields as much as 0.01 part of albumenoid ammonia per 100,000.

Reducing Power.—The absorption of less than 0.1 part of oxygen per 100,000 in the case of an upland surface water, and of less than 0.05 in the case of other waters, is usually regarded as indicating waters of satisfactory purity as regards organic matter. The result of any one determination is, however, rarely sufficient to condemn a water or to justify its use, and the amount of oxygen absorbed should be considered together with the yield of albumenoid ammonia.

Nitrite.—Nitrite may arise from the reduction of nitrate, but it occurs in sewage and manure, and it should be entirely absent from a drinking water.

Nitrate.—Nitrate, like chloride, is innocuous; but, as it is derived from nitrogenous organic matter of animal origin and is the final product of its decomposition, its presence in a water is an index of past pollution. It is not possible to fix a standard of purity in respect of nitrate, but a satisfactory surface water, even from cultivated land, seldom contains more than 1 part of nitrate (NO_3) in 100,000. Well water often contains a larger amount.

Acidity or Alkalinity.—If the relative acidity of a water is three to four times that of ideally pure water, the solvent action of the water on lead requires careful investigation.

Lead.—Drinking water should be entirely free from lead. On account of the cumulative nature of the poison, it is difficult to fix a limit to the amount of lead that is permissible in a water supply. If the amount never exceeds 0.03 part per 100,000, the water may probably be regarded as safe. A water supply which, under normal circumstances, is liable to contain up to 0.1 part of lead per 100,000 must be described as dangerous.

PART IX

QUANTITATIVE ANALYSIS OF ORGANIC SUBSTANCES

IN the analysis of organic compounds, the chief elements of importance that have to be considered are carbon, hydrogen, oxygen, nitrogen, the halogens, and sulphur.

Carbon and *hydrogen* are determined simultaneously after oxidation to carbon dioxide and water; *nitrogen* is obtained and measured in the free state, or is converted into ammonia; the *halogens* are converted into the corresponding silver or sodium salts; *sulphur* is determined as barium sulphate. There is no convenient, direct method of determining *oxygen*; it is found "by difference."

If *metallic radicals* are present, they are determined after oxidising the organic matter. The following method of oxidation is generally applicable. To a weighed quantity (about 2 grams) of the substance in a porcelain basin, 10 c.c. of concentrated sulphuric acid are added. The mixture is well stirred, and is heated on the steam-bath for ten minutes. A few drops of concentrated nitric acid are then added, the mixture is heated on a sand-bath until it begins to fume, and, at intervals of a few minutes, two or three drops of nitric acid are added. When the solution has become colourless, it is heated until it fumes strongly; it is then cooled, and the metallic radicals are determined in the usual manner.

CARBON AND HYDROGEN.

The determination of carbon and hydrogen is accomplished by a process of oxidation in which a known weight of the substance is burned in a current of air or oxygen and in

presence of copper oxide. The carbon and hydrogen are quantitatively oxidised to carbon dioxide and water, which are separately collected and weighed. The whole process is termed a "combustion."

The following apparatus is required:—

(1) **A Combustion Tube** of hard glass, 70 cm. long and 8 mm. internal diameter. The sharp internal and external edges at each end of the tube are rounded by heating carefully in a blowpipe flame. The tube is cleaned by drawing through it a plug of moist cotton wool attached

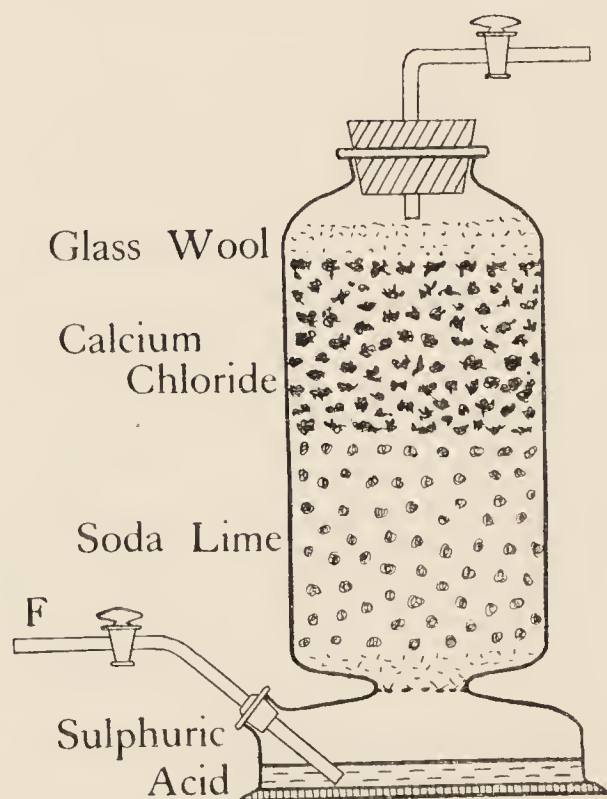


FIG. 85.

to a piece of string, and then rinsing with water. It is dried by warming and blowing a current of air through it.

(2) **A Heating Furnace** of the Dennstedt type, shown in Fig. 92, on p. 372. It consists essentially of an iron trough or gutter, 60 cm. long, supported on two uprights. The gutter is lined with asbestos cloth or fibre, and the combustion tube, which is laid in the gutter, is heated by three or four Bunsen burners provided with flame spreaders. Iron covers, lined with asbestos and supported on two angle irons, are placed over the tube during the combustion process.

(3) **A Purifying Tower** for removing moisture and carbon dioxide from the oxygen. This is shown in Fig. 85,

and should be about 30 cm. high and 10 cm. in diameter. The oxygen enters at F and passes first through sulphuric acid, next over granular soda-lime in order to remove carbon dioxide, and then over granular calcium chloride.

(4) **A Gas-holder** of about 5 litres capacity containing oxygen. The gas-holder (Fig. 86) is most conveniently filled from a cylinder of compressed oxygen. The gas must be free from traces of hydrogen.

(5) **Apparatus for the Absorption of Water and Carbon Dioxide.**

(a) The *water* formed in the combustion is absorbed in either calcium chloride or concentrated sulphuric acid. The most convenient form of calcium chloride tube is shown in Fig. 60, on p. 216. The tube is filled and any free lime or basic chloride in the calcium chloride removed by treatment with carbon dioxide, as described on p. 216. The carbon dioxide in the tube is displaced by passing *dry* oxygen through it for ten minutes, and the taps are then closed.

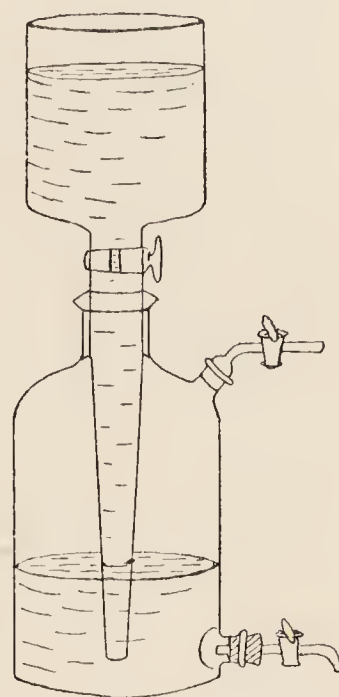


FIG. 86.

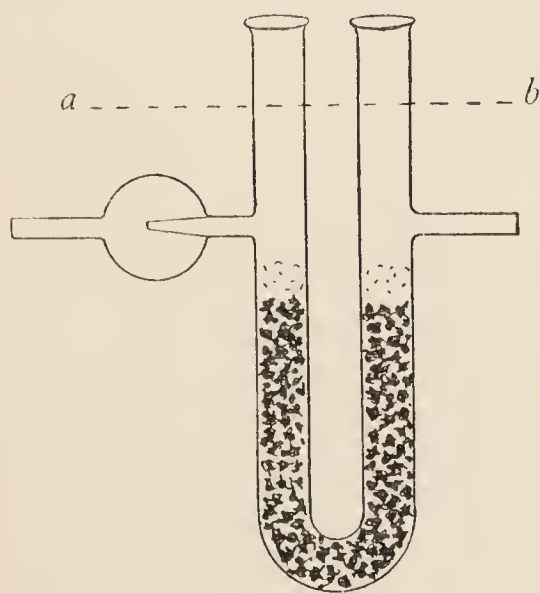


FIG. 87.

A rubber cap (or short piece of rubber tubing fitted with a plug of glass rod) should be provided for the purpose of closing the bulbed side-tube.

If sulphuric acid is to be used for the absorption of water, an unstoppered **U**-tube is required (Fig. 87). A quantity of granular pumice sufficient to fill the tube is soaked in concentrated sulphuric acid for a short time, the excess of acid is drained off,

and the pumice, contained in a porcelain basin, is heated in a good draught until fuming nearly ceases. The **U**-tube is then filled with the pumice to within 1 cm. of the side-tubes, and the tube is sealed in the blowpipe flame

at *a* and *b*. Concentrated sulphuric acid is then drawn into it through the shorter side-tube and, after the acid has been in contact with the pumice for about ten minutes, the excess of acid is drained off until the quantity that remains is *no more than sufficient* to fill the bend of the U-tube. The side-tube that has been in contact with the acid is then gently heated with a small flame until the acid that wets it is volatilised. The air in the tube is displaced by passing a current of *dry* oxygen for five minutes, and the tube is then closed with caps, fitted over the side-tubes and made from short pieces of rubber tubing closed with plugs of glass rod.

(*b*) For the absorption of the *carbon dioxide* formed in the combustion, two U-tubes (see Fig. 61, on p. 216) are required. A small wad of cotton wool is placed near the middle of one limb, and fine granular soda-lime is introduced so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb. The taps are made gas-tight with the minimum quantity of grease, and the air in the tubes is displaced by passing a current of *dry* oxygen for five minutes.

After the absorption tubes are filled, they are wiped with a dry cloth, care being taken to remove any grease exposed at the taps, and then placed in a cardboard box (Fig. 88) and taken to the balance-room, where they should remain for at least half an hour before weighing. Equilibrium with the moisture in the surrounding air will usually be more quickly established if the tubes, after wiping, are lightly breathed upon.

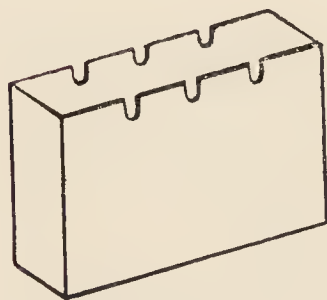


FIG. 88.

If the balance-pan is large enough, the tube may be laid upon it while the weighing is in progress, or it may be suspended from the hook of the balance by means of a stirrup made of aluminium wire, the combined weight of the tube and stirrup being, of course, recorded. If the pumice and sulphuric acid U-tube is used for the absorption of water, it *must* be suspended in this way. Before weighing, the rubber caps are removed from the side-tubes.

(6) **A Pulsimeter**, or indicator (Fig. 89), containing a few drops of concentrated sulphuric acid, is used to show the rate at which unabsorbed gas leaves the apparatus and to protect the calcium chloride in the last absorption tube from atmospheric moisture.

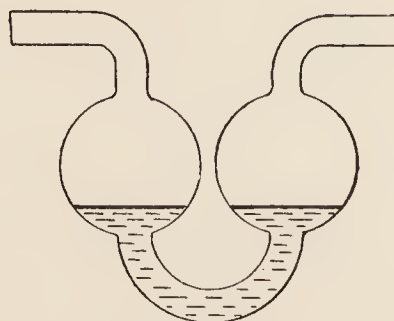


FIG. 89.

(7) **A Tube** (Fig. 90, A), about 20 cm. long and 2 cm. diameter, provided with a cork and calcium chloride tube. A constriction, into which the neck of the weighing-tube B exactly fits, is made near the open end of the tube A.

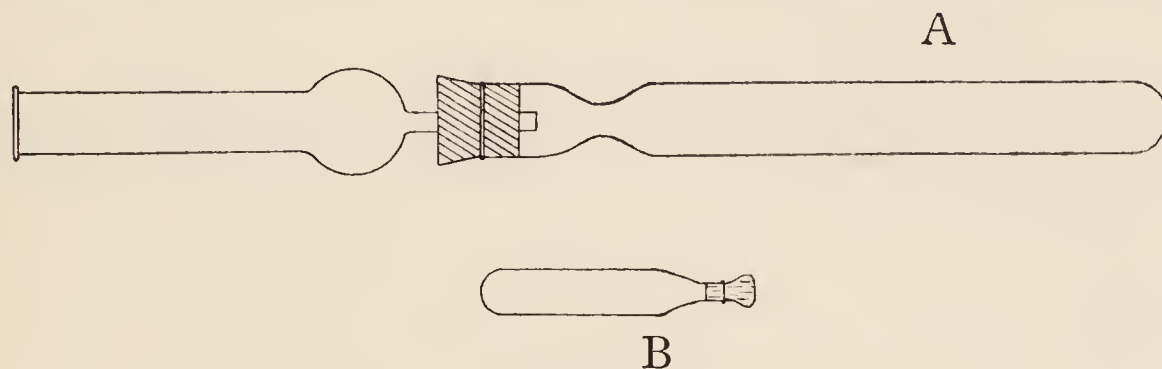


FIG. 90.

(8) **A Stoppered Weighing-tube** (Fig. 90, B), about 10 cm. long, the neck of which is of such a diameter as to fit into the end of the combustion tube. This tube may be made from a piece of glass tubing, and the stopper from a piece of glass rod ground into the neck by means of emery or carborundum powder.

Preparation of the Combustion Tube.

A quantity of wire-form copper oxide, sufficient to fill the combustion tube (30 to 35 grams), is carefully broken (not ground) in a mortar into somewhat smaller pieces, and is then sifted from dust through a 30-mesh sieve.

Another portion (about 15 grams) of the oxide is crushed until it is fine enough to pass through a 30-mesh sieve. This powder is then sifted, by means of a 60-mesh sieve, from fine dust, and the latter is rejected.

A short (2 cm.) roll of copper gauze, made by wrapping the gauze on a piece of copper wire with small loops at each end, is placed in the combustion tube about 15 cm. from one

end (Fig. 91, F). The tube is then charged with coarse copper oxide to within 22 cm. of the other end, and another copper gauze roll is used to keep the oxide in place. Fine copper oxide is then introduced until the tube is filled to within 8 cm. of the end. This is followed by a 2 cm. gauze roll. Another roll of copper gauze, 8 cm. long, is placed at the other end of the tube. The ends of the tube are fitted with rubber stoppers through which pass (at the end D) a small, straight calcium chloride tube, and (at the end E) a short piece of glass tubing which has been drawn out to a diameter of 3 mm. where it enters the stopper. The combustion tube is then laid in the furnace, and the end E is

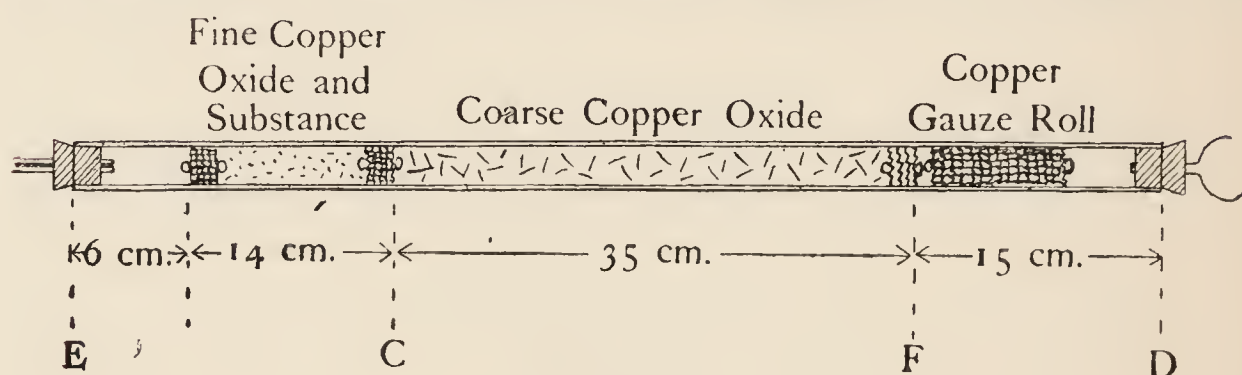


FIG. 91.

connected with the drying tower and oxygen supply by means of rubber tubing.

The gas burners are lighted, small flames being used at first, and, the covers having been laid in position, the tube is gradually heated to low redness, and a slow current of oxygen is passed through it. Care must be taken not to char the rubber stoppers, and, in order to protect them from the heat, two pieces of asbestos board provided with a hole and slit may be slipped over the ends of the tube. If any moisture condenses near the end D, the asbestos screen is removed for a time, or the end of the tube is gently warmed with a small flame until the moisture disappears. After the tube has been heated for half an hour, the oxygen current is stopped and the tube allowed to cool. The gauze roll at the end E is then withdrawn with a wire and placed on a clean watch-glass, and the fine copper oxide is transferred to the tube A which is at once closed with the calcium chloride tube. The gauze roll is replaced, and the combustion tube, which is now ready for use, is at once attached to the drying tower, or a calcium chloride tube is fitted into the end E.

Combustion of a Solid Substance containing Carbon and Hydrogen only, or Carbon, Hydrogen, and Oxygen.

The substance to be analysed must be perfectly dry. A small quantity, from 0.15 to 0.2 gram, is accurately weighed in the small stoppered tube B (Fig. 90). The substance is mixed in the tube B with a small quantity of copper oxide from A, and (having withdrawn the gauze roll from the end E of the combustion tube and placed it on a clean watch-glass) the mixture is transferred to the combustion tube. The tube B is then "washed out" several times with copper oxide, received as before from A, and emptied into the combustion tube, care being taken that nothing is lost in the process, and that the copper oxide is exposed to the air as little as possible. The mixture of copper oxide and substance should fill about 12 cm. of the tube, and is kept in place by means of the short roll of copper gauze. About 6 cm. of the tube remain unoccupied.

The following method of mixing the substance with fine copper oxide in the combustion tube is also convenient:—

A small quantity of copper oxide is first shaken into the combustion tube from the tube A, and the substance is introduced from the tube B (which is afterwards weighed again). More copper oxide is then added, in small portions at a time, and, after each addition, the substance and copper oxide are mixed by rotating the combustion tube.

The combustion tube is now laid in the furnace, and the end E is connected as before with the oxygen supply. The calcium chloride tube is removed from the end D, and the weighed absorption tubes are attached. The tubes are suspended, by means of hooks made of stout wire, from a rod fixed horizontally in a clamp. A rubber stopper, *which must fit the combustion tube accurately*, is pushed on to the bulbed side-tube of the calcium chloride U-tube (or the concentrated sulphuric acid U-tube), until the end of the side-tube is flush with the end of the stopper. The stopper is then tightly fixed into the combustion tube. (It is a good plan to lubricate the hole in the stopper by rubbing powdered graphite into it with a thin glass rod, the loose graphite being carefully removed; the stopper will then

slip on to the **U**-tube easily, and is easily removed again when the combustion is over. A trace of graphite rubbed on the surface of the stopper prevents it sticking to the combustion tube.)

The two soda-lime tubes are next attached, the limbs containing calcium chloride being in each case turned away from the combustion tube. The connections are made with short pieces of thick-walled rubber tubing (pressure tubing) lubricated with graphite, and the ends of the glass tubes should be brought close together inside the rubber junction. Wiring is unnecessary and should not be resorted to as a means of making the joints gas-tight. The pulsometer is finally attached in the same way, and the combustion proper commenced.

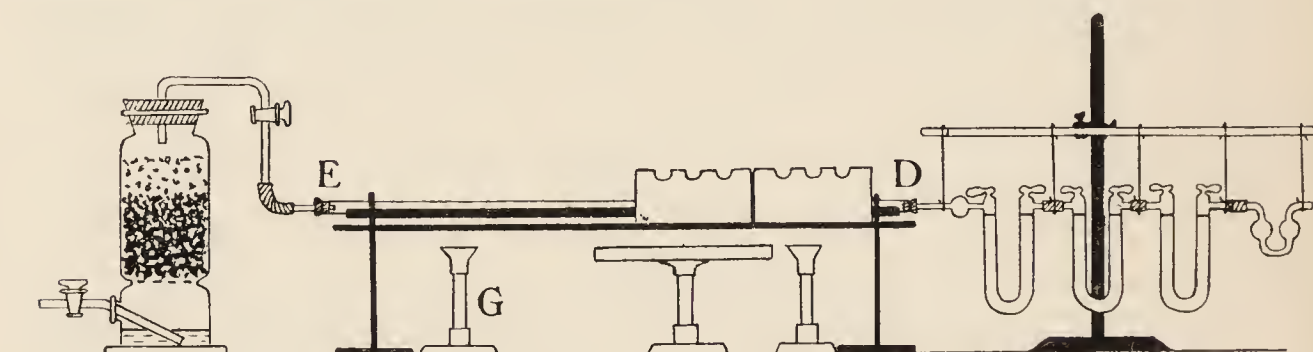


FIG. 92.—General Arrangement of Combustion Apparatus.

The taps of the **U**-tubes are opened and a current of oxygen is started at the rate of about one bubble per second, as seen in the pulsometer. The two burners under the front portion (Fig. 91, CD) of the tube are lighted, covers are placed over this part of the tube, and the temperature is gradually raised. The back portion of the tube is meanwhile protected from the heat as far as possible by means of a screen of asbestos board. When the copper oxide has attained dull redness, the third burner (G, Fig. 92) is lighted and placed under the gauze roll near the end E—no flame spreader being used at this stage. The flame, which is kept small at first, is gradually increased, and the burner is moved forward slowly, covers being placed over the tube behind the burner in order to keep the back portion of the tube hot. The substance burns for the most part in the moderately rapid current of oxygen, and, provided sufficient

oxygen is supplied, there is often little or no visible reduction of copper oxide to metallic copper. The first indication that combustion is taking place is the appearance of moisture at the front of the combustion tube, and, somewhat later, the heat that develops in the first soda-lime tube. The more volatile the substance subjected to combustion, the greater the care necessary in heating the back portion of the tube. If the heating is too rapid, incomplete combustion may result. A rush of gas through the pulsometer must be at once checked by removing the flame G for a time.

When the whole of the back portion of the tube has been carefully heated in this way, all the covers are laid in position, a flame spreader is placed on the burner G, and the whole tube is heated as uniformly as possible to *dull redness*. (If necessary, an additional burner may be used.) Any carbon that may have been formed by the decomposition of the substance is thus burned away. The temperature of the tube near the front cork must be carefully regulated with the help of the asbestos screen; if moisture tends to collect there, the screen should be removed for a time, or the tube warmed with a small flame until the moisture disappears.

Finally, when oxygen passes freely through the pulsometer and when the first soda-lime tube is practically cold, the combustion is finished. The burners are then extinguished and the absorption tubes detached. The taps are closed, and the rubber cap is replaced on the calcium chloride U-tube. The tubes are carefully wiped with a dry cloth, and, after an interval of not less than half an hour, are weighed. The fine copper oxide in the back portion of the tube is transferred to the tube A, and the combustion tube is at once closed at each end with a calcium chloride tube (the rear end may be left attached to the drying tower). The tube is then ready for the next combustion.

Example—

Weight of substance taken	0.1521 gram
Increase in weight of calcium chloride tube .	0.0684 „
Increase in weight of 1st soda-lime tube .	0.3828 „
Increase in weight of 2nd soda-lime tube .	0.0004 „

$$\text{Percentage of carbon} = 0.3832 \times \frac{3}{11} \times \frac{100}{0.1521} = 68.70$$

$$\begin{array}{rcl} \text{C}_7\text{H}_6\text{O}_2 \text{ (benzoic acid) requires} & \text{C} = & 68.82 \\ \text{Difference} & = & -0.12 \end{array}$$

$$\text{Percentage of hydrogen} = 0.0684 \times \frac{1.01}{9.01} \times \frac{100}{0.1521} = 5.04$$

$$\begin{array}{rcl} \text{C}_7\text{H}_6\text{O}_2 \text{ requires} & \text{H} = & 4.96 \\ \text{Difference} & = & +0.08 \end{array}$$

As a rule, the percentage of carbon found in a pure substance is a little below and that of hydrogen a little above the calculated values. The difference in each case should not exceed about 0.1.

The calcium chloride **U**-tube may be used for a large number of combustions without renewing the contents. The water that collects in the bulb should be drained off from time to time. The weight of the second soda-lime tube should remain practically constant. If a decided increase in the weight of the second soda-lime tube is observed, the soda-lime (but not the calcium chloride) in the *first* of these tubes should be renewed.

Combustion of a Liquid.

The liquid is weighed in a small bulb (Fig. 93) about 2 cm. long, provided with a fairly wide capillary 8 cm. long. The liquid is introduced by warming the weighed bulb and

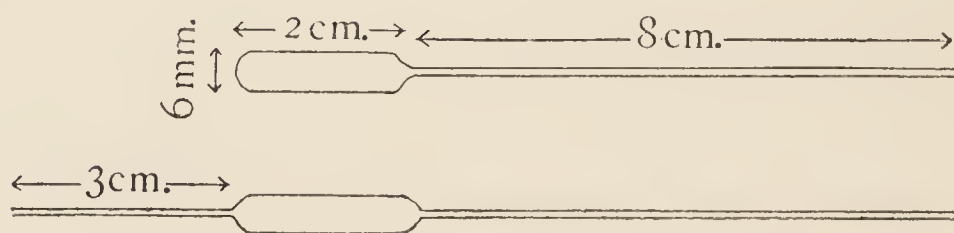


FIG. 93.

then allowing it to cool with the open capillary immersed in the liquid. Another convenient method is to place the bulb-tube, with the capillary immersed in the liquid, in a desiccator, which is then evacuated. On re-admitting air to the desiccator, the liquid is forced into the bulb. The capillary is gently warmed in order to drive out the liquid it contains, and is then sealed.¹ The tube and contents are then weighed.

¹ If the bulb-tube is to be placed in the combustion tube immediately after weighing, the capillary need not be sealed.

In the final weighing and subsequent handling of the bulb, care should be taken to prevent the liquid re-entering the capillary.

A file scratch is made near the tip of the capillary, the tip is broken off, and the bulb-tube, surrounded by copper oxide (received from the tube A, Fig. 90, on p. 369), is placed in the back part of the combustion tube with the open end of the capillary facing the current of oxygen. The combustion is started in the usual way, and, when the copper oxide in the front of the tube is hot, the liquid is slowly distilled out of the bulb into the copper oxide at the cool end of the tube by means of a small flame applied directly to the upper side of the combustion tube and over the bulb. The combustion is then continued as for a solid.

In the case of a decidedly volatile liquid, such as benzene, a bulb with a capillary at each end is used. The longer capillary (8 cm.) is plugged with fusible metal and the shorter (3 cm.) is sealed off in the usual way after the liquid has been introduced. Before the bulb is put into the combustion tube, the absorption tubes are attached and the front of the tube is heated to dull redness. The bulb is then pushed into the *empty*, cool part of the tube with the longer capillary facing the current of oxygen. The plug of fusible metal is then melted by the application of a small flame *above* the combustion tube, and the liquid is gradually vaporised by very gentle heating.

Modification of the Process if Nitrogen is Present.

If the substance contains nitrogen, the greater part of that element is liberated in the free state and escapes through the absorption tubes. Traces of nitrogen oxides, however, may be produced, and in order to prevent these oxides reaching the absorption tubes, they must be decomposed by passing them over hot copper. The copper gauze roll in the fore part of the combustion tube is removed, heated to low redness in a large flame, and dropped, while hot, into a test-tube containing about 0.5 c.c. of methyl alcohol. A clean, metallic surface is thus obtained. The roll is dried for about fifteen minutes in the steam-oven and then replaced in the combustion tube.

In the earlier stages of the combustion, the rubber tube connecting the combustion tube with the purifying tower is closed with a screw-clip—no oxygen being passed into the tube until the substance begins to burn and reduced copper oxide makes its appearance. Care must be taken, by keeping the copper oxide near the end E at dull redness, to prevent any unburnt substance reaching the cool, rear end of the tube. In other respects, the combustion is continued as described on p. 373.

Modification if Sulphur or a Halogen is Present.

If the substance contains a halogen or sulphur, combustion with copper oxide will yield volatile or unstable compounds of copper (copper halides and copper sulphate), and free halogen or sulphur dioxide will reach the absorption tubes and spoil the analysis. In both cases, the best method is to use fused, granulated, lead chromate instead of copper oxide in the combustion tube. The lead halides and lead sulphate are more stable and less volatile than the corresponding copper salts; but the temperature, especially in the extreme front portion of the tube, must not be too high. In the case of a halogen compound, a roll of silver gauze, placed in front of the copper oxide and kept at a moderate temperature, will usually retain any halogen.

NITROGEN.

Two methods are in common use for the determination of nitrogen in organic substances: (1) Dumas's method of combustion with copper oxide, in which the nitrogen, evolved as gas, is collected and measured; (2) Kjeldahl's method, in which the substance is decomposed by heating with concentrated sulphuric acid, whereby the nitrogen is converted into ammonium sulphate and is then determined as ammonia by the usual volumetric method. The first method is applicable to practically all types of organic compounds, and is generally preferred for scientific purposes. Kjeldahl's method is not suitable for hydroxylamine or hydrazine derivatives, or diazonium compounds. Nitrates, nitro-, nitroso-, and azo-compounds, and pyridine compounds require special treatment. The method is widely employed in commercial analysis.

Nitrogen by Dumas's Method.

The following apparatus is required :—

(1) **A Combustion Furnace and Combustion Tube** similar to those used for the determination of carbon and hydrogen. The combustion tube is charged with copper oxide as described on p. 369, and the copper roll, reduced with methyl alcohol (p. 375), is placed in the front end of the tube. There is no need to protect the copper oxide from atmospheric moisture, but it must be ignited in order to destroy organic matter.

(2) **A Hard Glass Test-tube**, 15 cm. \times 2 cm. This tube is nearly filled with sodium bicarbonate (free from ammonia), a plug of glass wool is inserted, and the tube, held horizontally, is tapped in order to form an air space above the substance. The test-tube is held in a clamp, and is connected with the rear end of the combustion tube by means of a V-shaped bulb-tube (Fig. 94) containing a globule of mercury. The mercury acts as an indicator of the rate at which the carbon dioxide passes into the

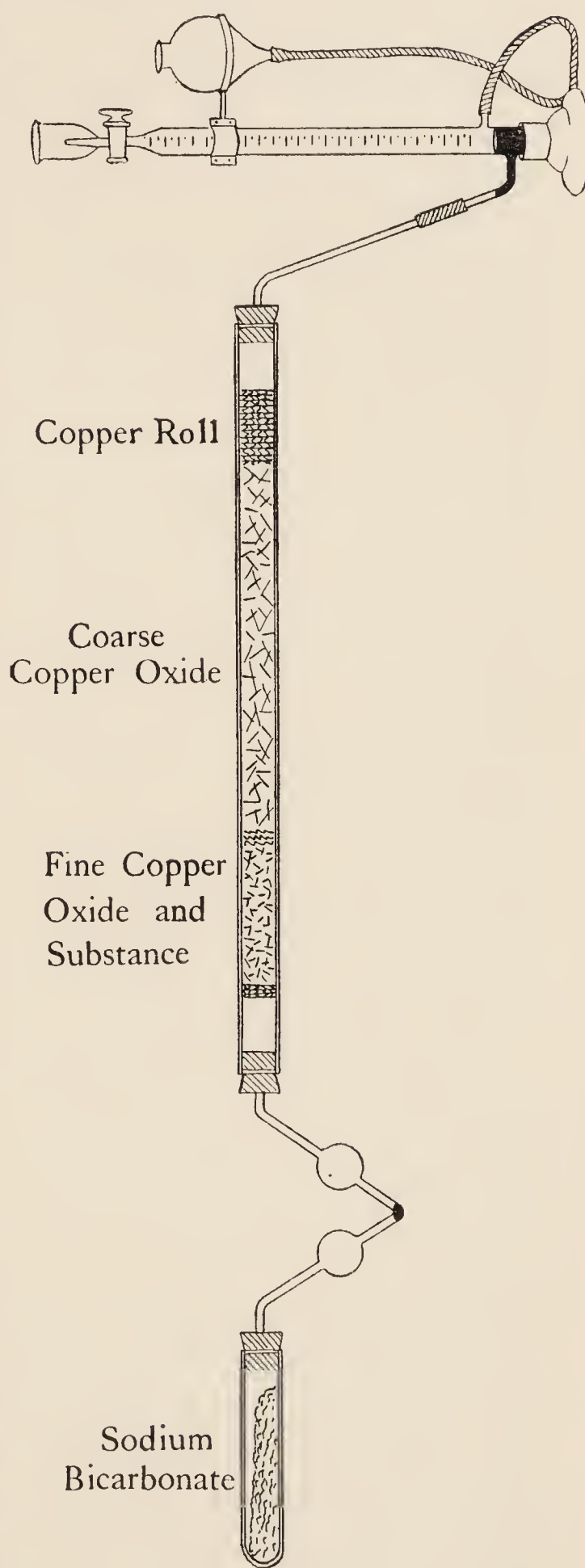


FIG. 94.

combustion tube when the sodium bicarbonate is heated. Over the test-tube is slipped a cylinder of wire gauze, which serves to distribute the heat somewhat, and prevents water condensing and cracking the hot glass.

(3) **A Nitrometer**, Fig. 94. Mercury is poured into the nitrometer until it stands about 5 mm. above the lower side-tube. The reservoir, clamped in its lowest position, is nearly filled with a 50 per cent. potassium hydroxide solution. In using the nitrometer, care must be taken that the caustic potash solution is not allowed to pass the mercury seal and to enter the side-tube that connects the nitrometer with the combustion tube; when the graduated tube is filled with the solution (by opening the tap and raising the reservoir), there must be sufficient mercury to prevent this. The rubber tube connecting the reservoir with the graduated tube must be wired on at each end.

Procedure.—If the substance is a solid, it is weighed in the tube B (Fig. 90) and, after being mixed with copper oxide, is transferred to the combustion tube in the manner described on p. 371. The amount of substance taken should be sufficient to yield 25 to 30 c.c. of nitrogen at the ordinary temperature, and it is useful to bear in mind that the volume of 1 milligram-atom (0.014 gram) of nitrogen at normal temperature and pressure is 11.2 c.c. The combustion tube is then laid in the furnace, and the rear end is connected with the sodium bicarbonate tube by means of the V-tube and accurately fitting rubber stoppers.

Before attaching the nitrometer, most of the air in the combustion tube is displaced by a fairly rapid current of carbon dioxide, obtained by heating the sodium bicarbonate tube with a small Bunsen flame. The flame is applied first at the closed end of the test-tube, and is gradually moved forward as the current of gas slackens. After the carbon dioxide has been passed for about five minutes, the burners under the front portion of the combustion tube are lighted, covers are placed over this part of the tube, and the nitrometer, with the tap open and the reservoir in the lowest position, is attached. The bent connecting tube is fixed into the combustion tube by means of an accurately fitting rubber stopper, and is attached to the side-tube of the nitrometer by

means of a short piece of pressure tubing which can be closed with a screw-clip.

In order to determine whether the air in the tube has been completely displaced, the potash reservoir is slowly raised, and, when the nitrometer is full of solution, the tap is closed and the reservoir lowered again. It is practically impossible to secure complete absence of residual air, but the bubbles that collect at the top of the nitrometer ought to be so minute that they appear as a foam or froth of inappreciable volume. If this is not the case, the nitrometer tap is opened, and the potash is run back into the reservoir, carbon dioxide is passed for several minutes more, and the test repeated.

When the result is satisfactory, the flame under the bicarbonate tube is lowered until the current of carbon dioxide is *very slow*, the nitrometer is filled with the potash solution, the tap closed, and the reservoir lowered as far as possible. When the front portion of the combustion tube has attained a dull-red heat, the burner under the rear end of the tube is lighted, and the mixture of copper oxide and substance is gradually heated in the same way as in a carbon and hydrogen combustion. The heating must be so regulated that the bubbles of nitrogen can be counted as they pass into the nitrometer. When the whole rear part of the tube has been heated, all the covers are laid in position, and the flame spreader is placed on the rear burner. When the evolution of gas becomes very slow, the residual nitrogen is expelled from the tube by a fairly rapid current of carbon dioxide (obtained by again heating the sodium bicarbonate).

Finally, when the bubbles of gas appear to be completely absorbed and the volume of nitrogen no longer increases, the nitrometer is detached by removing the cork from the combustion tube, and the screw-clip is closed. The reservoir is then raised until the surface of the liquid it contains is approximately level with that in the measuring-tube, and the nitrometer, with a thermometer hanging from the tap, is left for an hour in the balance-room or other cool place.

Before stopping the current of carbon dioxide, the front portion of the combustion tube is allowed to cool and the copper roll is removed. A current of oxygen is then passed

through the heated tube in order to oxidise the reduced copper oxide. After the tube is cold, the oxide in the rear portion is transferred to the tube A (Fig. 90, on p. 369).

The volume (v) of nitrogen obtained is then measured, after carefully equalising the levels of the liquid surfaces in the reservoir and measuring-tube, and the temperature (t) and barometric pressure (b) are noted. The vapour pressure (p) of the potash solution at t° will be found in a table on p. 425. The volume (V) of the nitrogen at normal temperature and pressure is then

$$\frac{v \times (b - p) \times 273}{760 \times (273 + t)},$$

and, since 1 c.c. of nitrogen at N.T.P. weighs 0.001250 gram, the percentage of nitrogen in the substance, if w is the weight taken, is

$$\frac{V \times 0.1250}{w}.$$

Instead of measuring the nitrogen over the potash solution—the vapour pressure of which, after partial

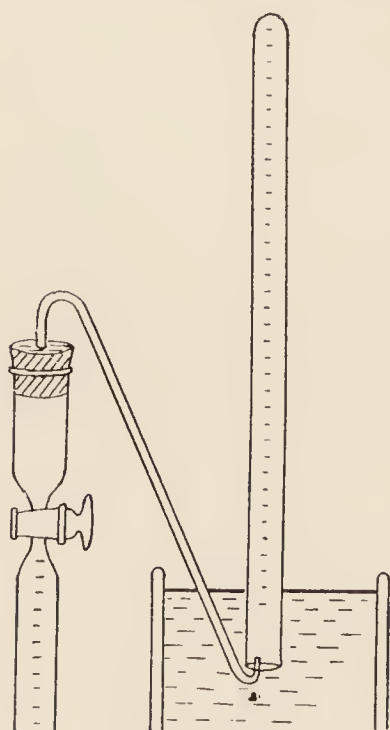


FIG. 95.

conversion into potassium carbonate, is somewhat uncertain—the gas may be transferred to a graduated tube filled with water, and standing over water contained in a tall cylinder. To accomplish this, the cup of the nitrometer is filled with water and a bent delivery tube, also filled with water, is attached by means of a rubber stopper (Fig. 95). No air should be present in the cup or delivery tube. The graduated tube is brought over the end of the delivery tube and clamped in position. On now raising the potash reservoir and opening the tap, the gas passes over into the

graduated tube. The tube is then immersed in the water for several minutes, after which the volume of the gas at atmospheric pressure is read. While adjusting the level of the water surfaces, the tube is held in a collar of paper.

The temperature of the gas is the temperature of the water, and the pressure is equal to the barometric pressure minus the vapour pressure of water (table on p. 425) at the temperature of observation.

The transference of the nitrogen to the graduated tube is greatly facilitated if a nitrometer of the type shown in Fig. 94 is used. The cup is filled with water; the graduated tube, filled with water, is placed over the small inner tube; and the nitrogen is driven into the graduated tube. The mouth of the tube is closed with the thumb, the tube transferred to a tall cylinder filled with water, and the nitrogen is measured as already described.

Nitrogen by Kjeldahl's Method.

OUTLINE OF METHOD.—The substance is decomposed by prolonged heating with concentrated sulphuric acid, whereby the nitrogen is converted quantitatively into ammonium sulphate. The ammonia is then determined by the usual volumetric method.

A Kjeldahl flask (Fig 96, A) is a round-bottomed, hard glass flask with a long, narrow neck; a loose stopper (B) for the flask is made by blowing a bulb on a piece of narrow tubing.

Procedure.—Place a weighed quantity of the substance in a *dry*, 100 c.c. Kjeldahl flask, care being taken that none of the substance adheres to the neck. (The amount of substance taken should be equivalent to 0.02–0.03 gram of nitrogen, *e.g.* 0.07 gram of oxamide, or 0.2 gram of acetanilide.) Add 10 grams of potassium sulphate and 20 c.c. of concentrated sulphuric acid (see, however, the Notes given below).

Support the flask on a piece of asbestos board (C) in which a hole about $1\frac{3}{4}$ inches in diameter has been cut. Heat the flask for a few minutes over a very small flame, and then increase the temperature so as to keep the liquid at

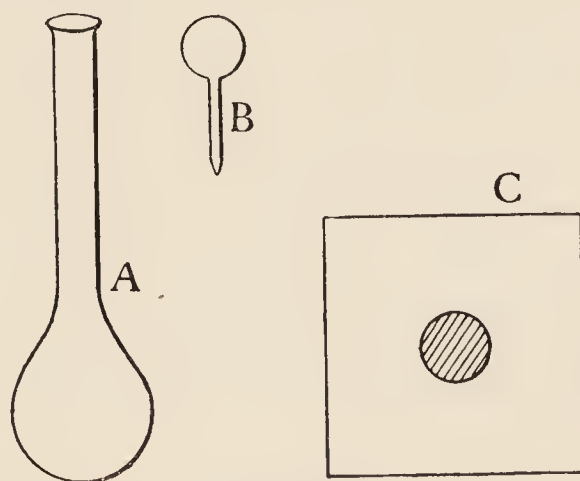


FIG. 96.

or very near its boiling-point until it becomes clear. (If no charring occurs, heat for one hour.)

Allow the flask to cool, and cautiously add sufficient water (about 50 c.c.) to dissolve the crystalline mass. Pour the solution into the copper flask of the apparatus described on p. 72, add the rinsings of the Kjeldahl flask, and dilute to 500 c.c. Add about 40 grams of sodium hydroxide ("sticks"), and connect the flask at once with the condenser. In the receiver place 25 c.c. of decinormal acid, and dilute with an equal volume of water. Boil until all the ammonia is expelled. Determine the excess of acid by titration with decinormal alkali, using methyl red as indicator, as described on p. 73.

Notes.—The time required for complete decomposition with sulphuric acid varies with the nature of the organic substance. The addition of potassium sulphate raises the boiling-point of the mixture and enables a higher temperature to be attained. The decomposition may be accelerated by the addition of 0.2 gram of mercury or copper oxide. (Potassium perchlorate is efficient as an accelerator, but appears to cause a slight loss of nitrogen.) If mercury is used, mercuri-ammonium salts are formed and must be decomposed by adding sodium sulphide (20 c.c. of a 4 per cent. solution) with the sodium hydroxide before distilling.

The reagents, especially the sulphuric acid, sometimes contain nitrogen compounds which may yield ammonia. A blank experiment must therefore be carried out with a substance containing no nitrogen (*e.g.* cane sugar), in order to ascertain whether any correction is necessary.

CHLORINE, BROMINE, AND IODINE.

In all the methods for the determination of the halogens in organic compounds, there is one common feature, *viz.*, the compound is decomposed in such a way that the amount of the halogen can be ascertained either gravimetrically by weighing the corresponding silver halide, or volumetrically by means of standard solutions of silver nitrate and ammonium thiocyanate. The methods differ in the manner in which the decomposition of the substance is effected.

Robertson's Method.

In Robertson's method the organic substance is heated with a mixture of chromic acid and sulphuric acid. Bromo-compounds are decomposed with evolution of bromine and a small quantity of hydrobromic acid; chloro-compounds yield chlorine, hydrochloric acid, and chromyl chloride. These volatile products are absorbed in alkaline hydrogen peroxide, and the alkali bromide or chloride is determined volumetrically. The method is widely applicable to bromo-

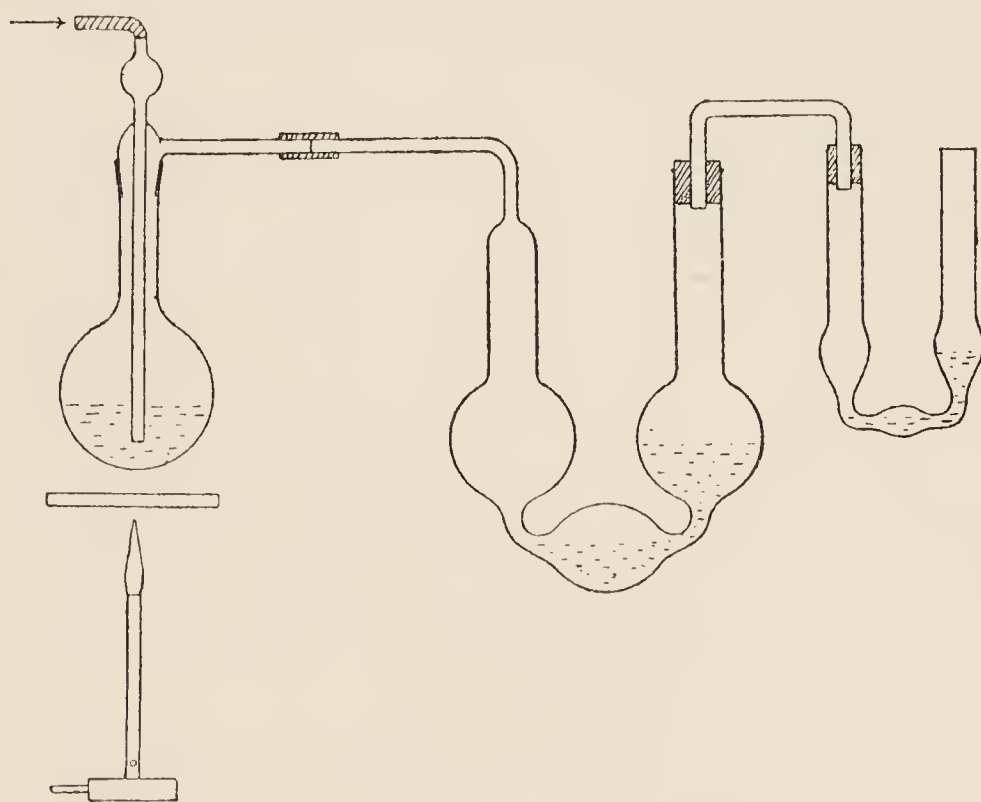


FIG. 97.

and chloro-compounds. It is not applicable to iodo-compounds, because a large quantity of the iodine is oxidised to iodic acid.

The Apparatus is shown in Fig. 97. The reaction vessel—a flask of about 100 c.c. capacity—is fitted with a ground-glass joint carrying inlet and exit tubes, and is heated by radiation from an asbestos gauze placed about 1 inch beneath it. The absorption vessels consist of two U-tubes provided with bulbs as shown in the diagram.

Procedure.—Place in the dry reaction vessel a weighed quantity of the substance equivalent to about 9 c.c. of decinormal silver nitrate, *i.e.* a quantity containing about 0.03 gram of chlorine or 0.07 gram of bromine. Introduce

from 6 to 8 grams of chromic acid. Place in position the ground-glass joint which has been lubricated with syrupy phosphoric acid. Connect the reaction vessel with the large absorption tube, measure into the latter from 10 to 15 c.c. of 10 per cent. sodium hydroxide solution and an equal volume of hydrogen peroxide, and then attach the small **U**-tube containing about 5 c.c. of sodium hydroxide. (These reagents ought to be free from chloride.) By means of a small funnel pour about 30 c.c. of concentrated sulphuric acid down the inlet tube into the reaction vessel, while aspirating a slow current of dry air through the apparatus.

Decomposition usually begins at once and should be checked by external cooling if it tends to become violent. Commence heating with a small flame, care being taken that the evolution of gas does not become rapid. After about ten minutes, when the initial vigour of the interaction has subsided, increase the flame and pass air somewhat more rapidly until, after about fifty minutes, the colour of the bromine or chromyl chloride vapour has disappeared and the decomposition is complete. Towards the end of the operation it is advisable to shake round the contents of the flask in case particles of incompletely decomposed substance have been projected above the level of the acid.

Transfer the contents of the **U**-tubes to a porcelain basin. In a bromine determination, acidify the solution with nitric acid, add 10 c.c. of decinormal silver nitrate, and titrate with standard (0.05 N) ammonium thiocyanate in the usual manner (p. 129).

If chlorine is being determined, heat the solution until boiling and acidify with nitric acid. (Heating is necessary in order to destroy the chromate which would obscure the end-point. The chromate is reduced to a chromic salt by the hydrogen peroxide and the solution becomes practically colourless.) Then add 10 c.c. of decinormal silver nitrate, stir well to coagulate the silver chloride, cool, filter, and wash. Titrate the filtrate with standard thiocyanate.

Correction for the presence of halogen in the reagents, etc.— As the reagents are seldom absolutely free from halogen, and since the hydrogen peroxide is not entirely without influence on the titration, it is necessary to ascertain the

correction that must be applied to eliminate these errors. The procedure is as follows:—Carry out a “blank” distillation (*i.e.* one in which the organic substance is omitted) under the same conditions and with the same quantities of reagents as in an actual determination. Transfer the contents of the U-tubes to a porcelain basin, add a weighed quantity (about 0.1 gram) of pure potassium bromide, and acidify with nitric acid. Add 10 c.c. of decinormal silver nitrate, and titrate with 0.05N thiocyanate. (It should be noted that in presence of the hydrogen peroxide the red colour of the ferric thiocyanate disappears in the course of several minutes.)

If 9.15 c.c. of the silver nitrate are actually required instead of 9.01 c.c. (calculated from the weight of potassium bromide taken), the difference (0.14 c.c.) must be deducted from the volume of silver nitrate required in any subsequent determination in which the same reagents are used.

Notes.—Pure potassium dichromate may take the place of chromic acid as the oxidising agent. A cold, freshly prepared solution of sodium peroxide, or a solution of sodium perborate (free from chloride) may be used as absorption reagent instead of a mixture of sodium hydroxide and hydrogen peroxide.

The results obtained with certain bromo-hydrocarbons are from 2 to 4 per cent. low, owing to volatilisation of some of the unchanged substance from the reaction mixture. For information regarding the modification of the procedure for those substances, etc., reference should be made to P. W. Robertson (*J. Chem. Soc.*, **107**, 902, 1915; *Chemical News*, **120**, 54, 1920).

Ter Meulen and Heslinga's Method.

In this simple method the organic substance is subjected to destructive hydrogenation by heating it in a current of hydrogen and ammonia. The halogen is obtained as the ammonium salt.

The Apparatus (Fig. 98) consists, in the first place, of a tube of hard glass (or transparent quartz), 80 cm. long and 1 cm. in diameter, a portion of which is heated to redness

in a short tube-furnace with 4 or 5 burners. Not less than half the length of the tube must extend beyond the furnace from C to D. The substance, contained in the boat B, is heated by a separate burner, and a mixture of hydrogen and ammonia is passed through the heated tube. The hydrogen is generated from zinc and dilute sulphuric acid in a Kipp's apparatus and is purified by passing it through two wash-bottles containing alkaline permanganate and acid permanganate respectively. The gas is then passed through concentrated ammonia solution in the wash-bottle E.

Procedure.—Weigh accurately in the boat from 0.02 to 0.05 gram of the substance. (Liquids are weighed in a small bulb drawn to an open capillary.) Place the boat in the tube at B and pass the hydrogen-ammonia current at

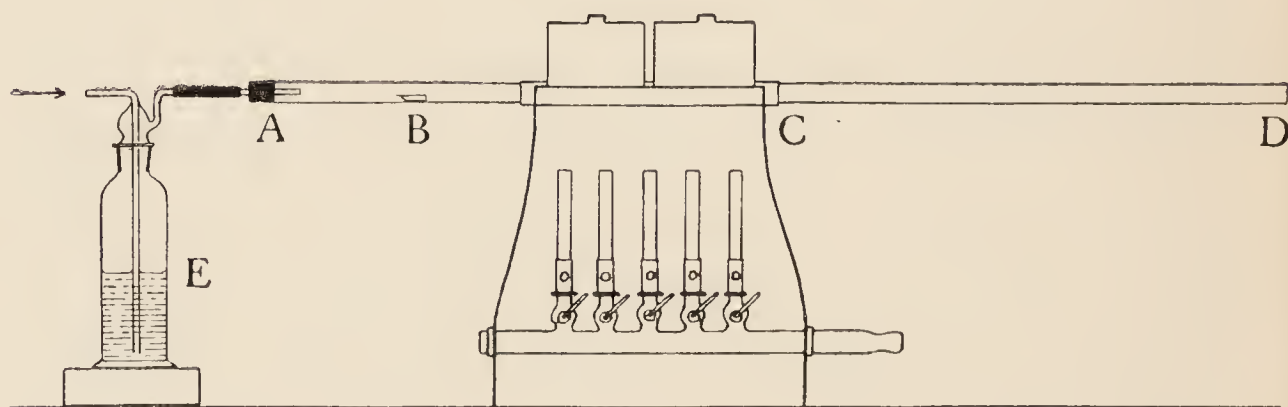


FIG. 98.

the rate of about two bubbles per second. Light the furnace after the air in the tube has been displaced. When the tube within the furnace has become hot, heat the tube between A and B with a small flame which is very gradually brought nearer the boat. Volatile substances must be heated very slowly. The ammonium salt is deposited as a sublimate just beyond the furnace. Care must be taken to avoid heating the sublimate so as to prevent the formation of fume or fog which would be carried away and lost. The decomposition of 0.05 gram of substance requires from thirty to forty-five minutes.

After complete decomposition, wash out the tube with the minimum quantity of water into a beaker. Acidify the solution with acetic acid and boil for a few minutes to decompose traces of ammonium cyanide. Determine the

halide volumetrically by means of standard (0.05 to 0.02N) silver nitrate and thiocyanate.

Note.—Full information regarding the analysis of organic compounds by destructive hydrogenation will be found in Thorpe and Whiteley's *Manual of Organic Chemical Analysis*.

SULPHUR.

The amount of sulphur in an organic compound may be ascertained by (a) oxidation of the sulphur to sulphate which is weighed as barium sulphate; (b) hydrogenation of the sulphur to hydrogen sulphide which is determined volumetrically.

Sulphur by Oxidation.

Except with volatile substances, the oxidation may be conveniently effected by means of sodium peroxide (Asboth's method).

Procedure.—In a porcelain basin mix together 9 grams of sodium peroxide and 6 grams of anhydrous sodium carbonate. Place 5 grams of the mixture in a nickel crucible, add a weighed quantity (0.2 to 0.5 gram) of the organic substance, and intimately mix the powders by stirring gently with a glass rod. Add the remainder of the oxidising mixture, and also "rinse" the glass rod with it.

Place the crucible in a hole cut in asbestos board and heat very gently until the contents shrink together; then raise the temperature gradually until the mixture forms a thin liquid. Remove the flame and, as soon as the contents of the crucible become solid, place the crucible upright in a 500 c.c. beaker containing about 50 c.c. of water. Cover the beaker and upset the crucible with a glass rod. Add more water and warm gently to decompose the sodium peroxide; then add excess of bromine water and heat on the steam-bath for at least thirty minutes. Remove the crucible and rinse it. Filter, and wash the residue with hot water. Acidify the filtrate (cautiously) with hydrochloric acid and evaporate to dryness on the steam-bath, in order to render

the silica (derived from the glass vessels) insoluble. After removal of the silica, determine the sulphate as described on p. 170.

Sulphur by Hydrogenation.

The hydrogenation is effected by the destructive distillation of the substance in a current of hydrogen in presence of finely divided platinum. The hydrogen sulphide formed is absorbed in sodium hydroxide solution (Ter Meulen's method).

The Apparatus (Fig. 99) consists essentially of a tube of

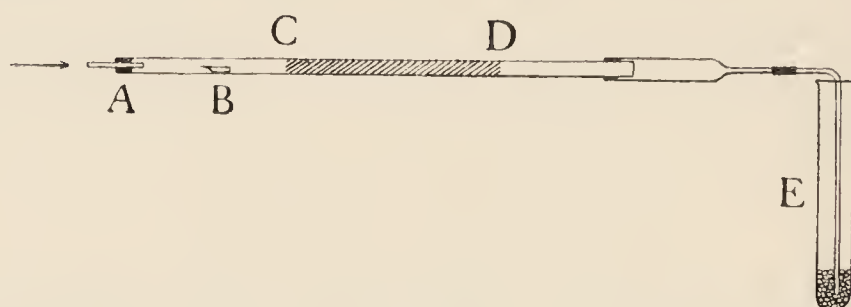


FIG. 99.

hard glass (or transparent quartz), 40 cm. long and 1 cm. in diameter; the portion C to D (16 cm.) is filled with platinised asbestos which is heated in a short tube-furnace similar to that shown in Fig. 98. (The platinised asbestos is prepared by moistening short-fibre asbestos with hydrochloroplatinic acid solution, then drying and igniting.) The substance is placed in the boat B, and the tube E contains glass beads and sodium hydroxide solution. A Kipp's apparatus to supply purified hydrogen (see p. 147) and another for carbon dioxide are also required.

Procedure.—Weigh accurately in the boat from 0.02 to 0.03 gram of the substance. Displace the air in the tube with a current of carbon dioxide. Cover the glass beads in the tube E with dilute sodium hydroxide solution. Remove the cork A, quickly introduce the boat, and connect at once to the supply of purified, *air-free* hydrogen. Pass the hydrogen through the tube at the rate of two bubbles per second. Light the furnace and heat the catalyst to dull redness. Then heat the tube between A and B with a small flame which is very gradually moved nearer the boat. The hydrogenation of 0.03 gram of substance requires about thirty minutes.

When the hydrogenation is complete, transfer the contents of the tube E to a flask containing a slight excess of decinormal iodine and more than sufficient acid to neutralise the alkali. Rinse the tube with air-free water. Titrate the excess of iodine with standard thiosulphate.

Notes.—Substances that char very much when heated must be mixed with 0.5 gram of platinum black. (The platinum black is made by reducing ammonium chloroplatinate with hydrogen; it may be used repeatedly by heating it to redness after each analysis.)

The carbon deposited on the catalyst and on the walls of the tube during the hydrogenation may be removed and the tube made ready for another analysis by heating it in a current of air after displacing the hydrogen by carbon dioxide.

PART X

THE DETERMINATION OF MOLAR WEIGHTS

IT is often necessary, more particularly in organic analysis, to determine which multiple of the empirical formula of a substance represents its *molecular* formula. Obviously, a rough approximation to the true molar weight is sufficient for this purpose.

Whenever possible, the molar weight should be determined by two or more methods, since the molecular complexity of most substances is not the same under all conditions. For example, the molar weight of benzoic acid in most solvents is about 122, in agreement with the formula $\text{C}_6\text{H}_5\text{COOH}$; but in benzene solution its molar weight is about 240, and its formula is therefore $(\text{C}_6\text{H}_5\text{COOH})_2$. The molecular complexity of a dissolved substance frequently depends on the nature of the solvent.

The chief methods in common use for determining molar weights are based on the determination of (1) the vapour density; (2) the freezing-point of a solution of the substance; and (3) the boiling-point of a solution of the substance. The vapour density method has the advantage over the other methods that no solvent is used, and it gives the molar weight of a substance in the gaseous state; the other methods give the molar weight of the dissolved substance.

DETERMINATION OF VAPOUR DENSITY AND MOLAR WEIGHT.

The molar weight of a gas is the weight of the gas, in grams, that occupies 22.4 litres at 0° and 760 mm. Provided a substance can be converted into vapour, the molar weight of its vapour can be ascertained by measuring its vapour density. The practical problem resolves itself into finding the volume, temperature, and pressure of a known weight of the substance in the state of gas. This can be done most conveniently, and with an accuracy sufficient for ordinary purposes, by either Victor Meyer's (constant pressure) or Lumsden's (constant volume) method.

CONSTANT PRESSURE METHOD.

OUTLINE OF METHOD.—A known weight of the substance is converted into vapour in a suitable apparatus, and, the pressure being constant (equal to that of the atmosphere), the *increase in volume*, due to the formation of the vapour, is determined. In other words, the volume of a known weight of the substance, measured under definite conditions of temperature and pressure, is ascertained. It is then easy to calculate the molar weight of the substance.

The Apparatus (Fig. 100) consists essentially of a tube A in which the substance is vaporised, and a burette B in which the air displaced by the vapour of the substance is measured. The tube A is provided with two side-tubes C and D. C is connected with the burette by means of a glass tube about 18 inches long. The tap H is convenient, but is not essential. A glass rod passes through the side-tube D, the joint being made air-tight by means of a piece of rubber tubing wired on *over* both rod and tube. The open end of A is closed with a rubber stopper E. The burette is connected with a levelling-tube fitted with a jet and spring clip.

The bulb A must be heated to a temperature at least 25° higher than the boiling-point of the substance under investigation. If the boiling-point of the substance is below 75°, the heating is most conveniently performed by means of steam, using the jacket shown in Fig. 102, on p. 395.

If the substance boils at a temperature above 75° , steam cannot be used as a source of heat. The apparatus shown

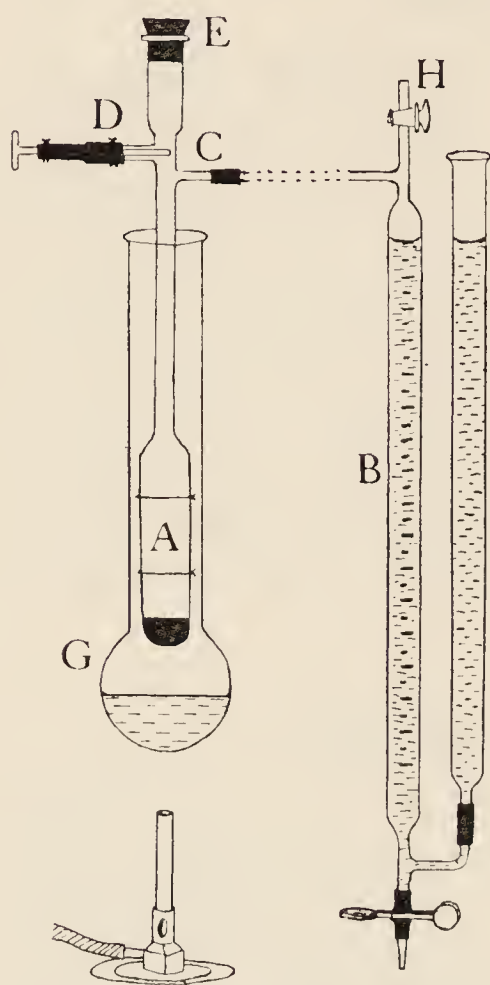


FIG. 100.

in Fig. 100 must then be used. A suitable liquid is boiled in the tube G with such vigour that its vapour nearly fills the tube. Aniline (boiling-point 184.4°), nitrobenzene (boiling-point 211°), quinoline (boiling-point 238°), and α -bromnaphthalene (boiling-point 279°) are useful heating liquids. For still higher temperatures, the apparatus must be made of hard glass or of silica. Sulphur (boiling-point 445°) or other substances of high boiling-point may be used, but it is usually preferable, for very high temperatures, to use a bath of molten metal, *e.g.* tin (melting-point 232°). In this case the bulb must be completely immersed in the heating liquid and the

temperature must be kept constant, although, so long as it is high enough, it is not necessary to know what the temperature is.

In order to protect the bulb A from fracture when the weighing-tube is dropped into it, a quantity of mercury should be placed in the bulb; the mercury also greatly accelerates the rate of vaporisation of the substance. At temperatures above 150° , fusible metal, or a small pad of asbestos fibre, should be used instead of mercury.

The upper part of the tube A is protected from the heat by means of a piece of asbestos board resting on the top of the tube G. In order to prevent the tube A from touching the wall of the outer vessel, two pieces of string may be tied round the bulb. The tube A is supported within the vapour jacket by means of a cork fitted into the top of G. After boring the cork, it must be cut into halves, and a groove should also be cut in the side in order to allow air to escape from G when heat is applied.

The substance is weighed in a narrow tube, about 1 inch long, of thin glass (Fig. 101). This tube is not stoppered, but is provided with a cap, which is removed just before the tube is dropped into the apparatus. With a little care, this arrangement is quite satisfactory even with a very volatile liquid such as ether. It is convenient to fix the tube into a piece of cork during weighing.

Procedure.—Clean the tube A and dry it carefully by warming and blowing a current of air into it. Pour into the tube about 10 c.c. of dry mercury and place it inside the vapour jacket. Almost fill the burette and levelling-tube with water, and connect the burette with A. Hang a thermometer close to the burette.

Insert the cork E, open the tap H, and boil the liquid in G (or pass a fairly rapid current of steam, if the steam jacket shown in Fig. 102 is used).

Meantime weigh accurately a suitable quantity of the substance (*e.g.* about 0.08 gram of acetone) in the small tube. Then close the tap H, and note whether the level of the water in the burette remains unchanged during the next minute or so. If not, open H again, and after a few minutes repeat the test. When constant temperature is attained, open the tap H, remove the stopper E, and read the burette. Carefully drop the weighing-tube, without the cap, on to the rod at D, replace the stopper E, and close H. Then, by moving the rod D, allow the tube containing the substance to drop to the bottom of A. The liquid quickly vaporises. As the air that is expelled from A passes over into the burette, run off water at the jet so as to keep the levels of the water in the burette and levelling-tube about the same; error through leakage is thus minimised. In about a minute or less, expansion ceases and the volume of air in the burette becomes constant. Now equalise the water levels, in order to bring the air in the burette under atmospheric pressure, and read the burette. Note the temperature and ascertain the height of the barometer.

The difference between the burette readings gives the volume of air equal to the volume of the vapour, measured

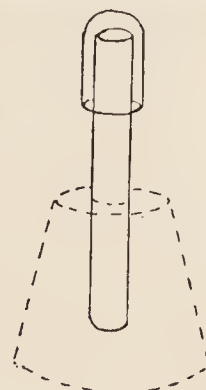


FIG. 101.

Weighing-tube
and cap (full
size).

at room temperature and atmospheric pressure. Calculate what this volume would be at 0° and 760 mm., and then find what weight of the substance, if it were a gas, would occupy 22.4 litres at normal temperature and pressure. This is the molar weight of the substance.

Precautions and Notes.—The substance must vaporise quickly, otherwise part of the vapour may, by diffusion, reach the upper and colder portion of the tube and condense there. Since the displaced air is measured over water and is saturated with moisture, a correction may be applied for the vapour pressure of water; but, since the air before displacement may be assumed to be half saturated, only half the vapour pressure of water at the room temperature (p. 425) should be deducted from the barometric pressure.

At the conclusion of an experiment, a glass tube is passed down into the bulb A, and the vapour is removed by means of the water-pump. Another weighing-tube containing a fresh portion of the substance, is then dropped in as before.

CONSTANT VOLUME METHOD.

OUTLINE OF METHOD.—A known weight of the substance is vaporised in an apparatus of constant volume and the *increase of pressure*, due to the formation of the vapour, is measured. If the temperature of the vapour and the volume of the apparatus are known, the molar weight of the vapour can be calculated.

The Apparatus (Fig. 102) is similar to that used in Victor Meyer's method, but the tube A may be much shorter, and a manometer M takes the place of the burette. The manometer is graduated in millimetres, and contains sufficient mercury to fill it almost to the top of the graduated portion when the meniscus in the other limb is at a fixed mark B. The position of this mark determines the volume of the vaporisation tube. In order to heat the bulb A, either a closed tube (Fig. 100) or a steam jacket¹ (Fig. 102) is used.

¹ The steam used should be dry. The water-trap shown at the side of the diagram is simple and efficient. The clip on the waste pipe is opened sufficiently to run off the water without allowing much steam to escape.

The volume of the vaporisation tube is found by weighing the tube empty and then full of water. It is unnecessary, however, to know the volume of the tube or the temperature of the heating jacket—provided these are maintained constant during the experiment—and the following method of

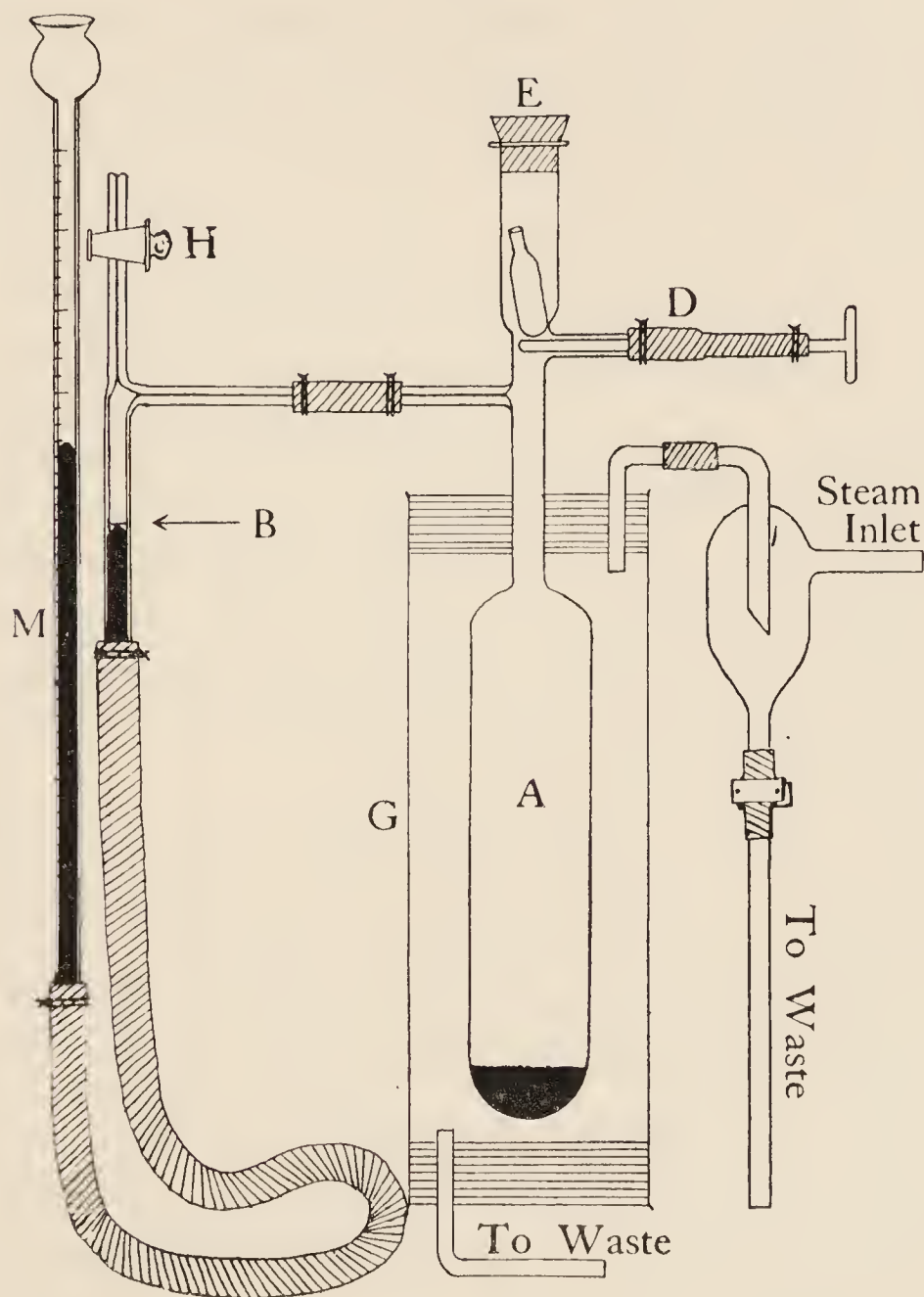


FIG. 102.

procedure is convenient, especially for high temperatures, when it is easier to keep the temperature constant for a time than to determine exactly what the temperature is.

First determine the increase of pressure produced by vaporising a known weight of a substance of *known* molar weight, and calculate from this the increase of pressure that would be observed if a gram-molecule, or

mole, of the substance were used. [In the same apparatus (*i.e.* in the same volume) and at the same temperature of vaporisation, a mole of any substance would give the *same* increase of pressure—a constant that may be regarded as the **molar increase** of pressure for the apparatus.] Then determine the increase of pressure produced by vaporising a known weight of the substance under investigation, and from this calculate what weight of the substance would give a pressure equal to that produced by one mole of the known substance, *i.e.* equal to the constant molar increase of pressure for the apparatus. If w grams of a substance produce a rise of pressure p , the molar weight of the substance is equal to $K \frac{w}{p}$, where K is the “molar increase.”

Procedure.—Clean and dry the tube A and pour into it about 15 c.c. of mercury. Fill the manometer with mercury, fit the apparatus together, and start the preliminary heating—the tap H being open. Clamp the manometer in such a position that the mercury stands at the mark B. When temperature equilibrium is attained, the mercury will remain at the mark when the tap H is closed.

Weigh accurately in the capped tube (Fig. 101) a quantity of a substance (of known molar weight) sufficient to give a rise of pressure of 100 to 200 mm. (*e.g.* about 0.08 gram of acetone, if the volume of the tube A is about 200 c.c.). Drop the tube (without the cap) on to the rod at D, replace the stopper E, and close the tap H. Let the tube and contents fall into the bulb, and, as vaporisation proceeds, slowly raise the tube M in order to keep the mercury near the mark B. In less than a minute the vaporisation is complete and the mercury becomes stationary. Now place the manometer tubes close together, and carefully adjust and clamp the tube M so that the mercury stands at the mark B. Read the position of the mercury in the tube M, and also note the graduation at the level of the mark B, *i.e.* find the distance in millimetres between the two mercury surfaces. This is the increase of pressure produced with a known weight of the substance, and it is easy to calculate the increase that would have been observed if one mole had been used.

Now cautiously open the tap H and at the same time lower the tube M, and remove the vapour from the apparatus by means of a current of air. Repeat the experiment with the same substance several times, and take the mean of the results as the "molar increase."

Having in this way "standardised" the apparatus, determine the increase of pressure produced by a known weight of, for example, methyl iodide, methyl alcohol, chloroform, or ether, and calculate the molar weight of the substance.

THE FREEZING-POINT METHOD.

The freezing-point of a solution is always lower than that of the pure solvent and, with dilute solutions, the depression of the freezing-point is proportional to the concentration of the dissolved substance.

If s grams of a substance dissolved in w grams of a solvent lower the freezing-point of the solvent Δ° , the molar weight, M , of the substance may be calculated from the formula,

$$M = K \frac{s}{\Delta w}$$

where K is a constant depending on the nature of the solvent. K is one thousand times the depression of the freezing-point that would be observed with a solution containing 1 mole of a substance dissolved in 1000 grams of the solvent. The value of K for a given solvent may be experimentally determined by observing the depression produced by a substance of known molar weight, or it may be calculated from the latent heat of fusion of the solvent. The constants for the commonest solvents are given in the following table:—

<i>Solvent</i>	<i>Freezing-point</i>	<i>K</i>
Acetic Acid . . .	17.5°	3880
Benzene . . .	5.49°	5000
Bromoform . . .	7.6°	14400
Water . . .	0°	1870

It is often convenient to use a known *volume* of the solvent

instead of a known *weight*. The molar weight can then be calculated from the formula,

$$M = k \frac{s}{\Delta v}$$

where v is the volume in cubic centimetres at 15° of the solvent. The values for k are as follows:—

Acetic Acid	3700
Benzene	5650
Bromoform	5100
Water	1870

These formulæ hold true only when the solvent separates in a pure state; the freezing-point method for determining molar weights cannot be used, therefore, if the solvent and solute form mixed crystals.

The Thermometer.—The above formula for the calculation of molar weights is applicable only to experiments with *dilute* solutions, with which the observed depression of the freezing-point is a small fraction of a degree; *e.g.* addition of one-tenth of a mole of a substance per litre depresses the freezing-point of water by only 0.187° .

For most purposes, however, it is sufficient to determine molar weights accurate to within 5 per cent. The formula can be applied, with about this degree of accuracy, to experiments with solutions up to 0.5 mole per litre, corresponding to a depression of 0.9° with water and 2.5° with benzene. For this type of work, a thermometer graduated in tenths or twentieths of a degree, and with an open scale that can be read to hundredths, is sufficiently accurate.

For more accurate work, a Beckmann thermometer (see p. 402) must be used.

The Apparatus (Fig. 103) consists of a large test-tube A, provided with a side-tube B, and placed inside a wider tube C, so as to be surrounded by an air-jacket. The wider tube C is supported by the metal cover of the cooling-bath D, and it is convenient to weight the tube with shot so that it will not float. The freezing-point tube A is fitted with a cork carrying the thermometer and a short glass tube through which the stirrer S can pass freely. The

stirrer S is made of stout nickel wire (or of glass if the liquid attacks nickel), and is provided with a cork handle to prevent conduction of heat.

The temperature of the cooling-bath must be kept from 3° to 4° below the freezing-point of the solvent; an ordinary thermometer is placed in the cooling-bath, and the temperature is observed from time to time to make sure that this condition is observed. For experiments with water as solvent, a mixture of ice and concentrated brine may be used; for experiments with benzene, the cooling-bath may be kept at about 2° by the use of water to which a few lumps of ice are added occasionally. The level of the liquid in the cooling-bath should be about an inch higher than the level of the liquid in the freezing-point tube. The mixture in the cooling-bath must be stirred occasionally.

Determination of the Molar Weight of a Substance in Benzene.

Clean and dry the freezing-point tube. By means of a dry pipette introduce 20 c.c. of *pure* benzene, and arrange the apparatus as shown in Fig. 103. The dimensions of the freezing-point tube should be such that with 15 to 20 c.c. of liquid the top of the thermometer bulb is at least 7 mm. below the top of the liquid, and the bottom of the bulb at least 7 mm. from the bottom of the freezing-point tube.

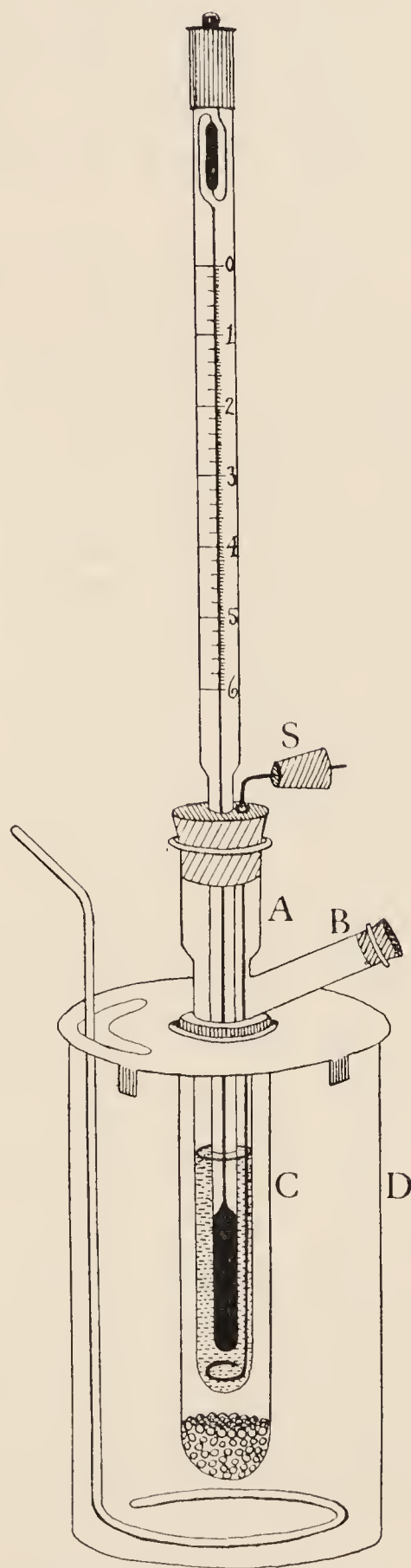


FIG. 103.

If a weight measurement of the solvent is desired, attach a piece of fine wire to the neck of the tube so that it can be suspended from the hook of the balance. Weigh the dry tube, and weigh again after the addition of from 14 to 18 grams of benzene. It is sufficient to weigh to the nearest centigram.

First determine the freezing-point of the pure solvent as follows:—

Place the freezing-point tube directly in the cooling-bath, and stir the benzene steadily until the temperature falls to about 6° . Then remove the tube from the bath and, after drying the exterior, place it at once within the tube C. Stir very slowly until the temperature falls to about 5.1° , and then stir vigorously in order to induce crystallisation.¹ As soon as the freezing commences, the temperature rises quickly. From this point stir steadily—but not vigorously—and observe the temperature as accurately as possible with the aid of a lens until it becomes constant. In order to reduce the “accidental” error of experiment, determine the freezing-point three times, and take the mean value. In making a second or third observation of the freezing-point, remove the tube with the thermometer and fittings from the wider tube, and warm it with the hand until almost the whole of the crystals have melted. Replace the tube and stir the liquid. The remaining crystals melt before the liquid begins to cool again. Proceed as in the first measurement of the freezing-point.

When the freezing-point of the solvent has been ascertained, add a weighed quantity of the substance. As it is desirable to determine the freezing-points of solutions of different concentrations, place about 1 gram of the substance in a small stoppered weighing-tube, and weigh. Empty from 0.05 to 0.20 gram of the substance (sufficient to give a depression of about 0.3°) into the freezing-point tube, and find the exact weight added by re-weighing the tube and contents.

¹ The solid solvent must separate in fine crystals. The formation of solid crusts on the side of the tube may be caused by (1) inefficient stirring; (2) too rapid cooling, either from the bath being kept at too low a temperature or from lack of a sufficient air-space round the freezing-point tube; or (3) use of a dirty tube.

Solids that cannot conveniently be introduced in the form of powder should be made into small pellets or tablets by means of a tablet press.¹ Several of these tablets are placed in the weighing-tube, weighed, and one or more added according to size. Liquids are weighed in a small pipette of the form shown in Fig. 104. A piece of rubber tubing is attached to the end E, and a portion of the liquid is transferred to the freezing-point tube by blowing. The pipette is then weighed again.

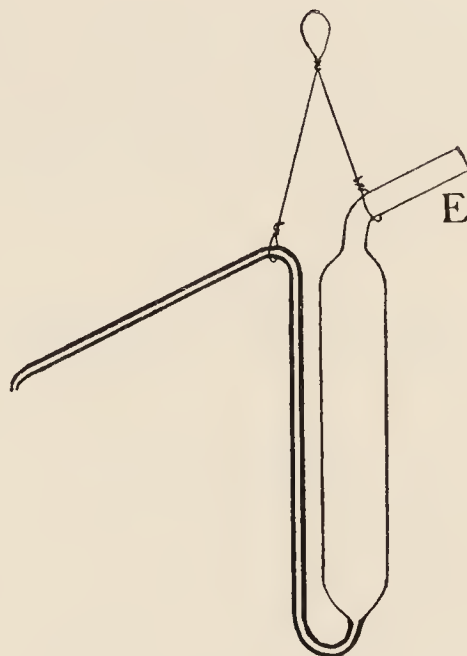


FIG. 104.

Having introduced the substance, stir vigorously (holding the tube at an angle of about 45°) until it has completely dissolved. Then place the tube directly in the cooling-bath, and stir the liquid at intervals until it begins to freeze. Remove the tube from the bath and, after drying the exterior, warm with the hand until only a few crystals remain unmelted. Replace the tube in position within the wider tube C. From this stage, proceed according to the directions given for determining the freezing-point of the pure solvent. The temperature rises at first for perhaps a minute, during which period the remaining crystals melt; it then falls steadily until crystallisation begins, when it rises quickly to the freezing-point of the solution, and then begins to fall again slowly.

The supercooling, *i.e.* the amount that the temperature falls below the freezing-point before crystallisation begins, must not exceed 0.5° ; if it does, the observed freezing-point may be used as a guide for the next experiment, but must not be used for the calculation of the molar weight. The highest temperature reached after the crystallisation begins is taken as the freezing-point. If simple stirring is not sufficient to induce crystallisation before the supercooling

¹ The "Pigmy" tablet-making machine, used by pharmacists, is convenient for this purpose.

exceeds 0.5° , a nucleus of the solid solvent must be introduced through the side-tube. Some benzene is frozen in a small test-tube and, by means of a glass rod (cooled in the same test-tube), a minute fragment of the solid solvent is brought into contact with the lower end of the stirrer when the supercooling amounts to about 0.3° .

Determine the freezing-point at least three times, thawing the frozen material after each measurement, as described above. Add further weighed portions of the substance, find the freezing-point after each addition, and from each set of data calculate the molar weight.

Modifications of the above Procedure if a Beckmann Thermometer is used.

The Beckmann thermometer is described below, but it will be convenient to mention here certain modifications of the above procedure that are necessary if a Beckmann thermometer is used. The ordinary Beckmann thermometer may be read without difficulty—so far as the mere scale reading is concerned—to $\frac{1}{1000}^{\circ}$. This is apt to lend a spurious appearance of accuracy to experiments with a Beckmann thermometer since, in reality, it is a matter of difficulty to obtain temperature measurements with it accurate to $\frac{1}{100}^{\circ}$. The more important sources of error are—

- (1) The ease with which the bulb is deformed and its volume consequently altered. This may occur during an experiment even with careful handling.
- (2) The inaccuracy of the scale, *i.e.* 1° on the scale may be either more or less than a degree. The scale is often inaccurate and uneven, and, even if it is accurate at one temperature, it cannot be quite accurate at any other temperature for which it is necessary to re-set the thermometer, since this involves alteration of the amount of mercury in the bulb.
- (3) The large heat capacity of the bulb.
- (4) The “sticking” of the mercury in the very fine capillary of the thermometer.

Apart from the first, these errors can be eliminated either by suitable modifications of the procedure or by introducing the necessary corrections. This, however, greatly complicates the process, and, as highly accurate measurements are rarely required, it is sufficient for most purposes to adopt only the following modifications of the procedure already described.

- (1) The amount of solvent taken should be from 20 to 25 grams. The bulb of the thermometer must be immersed to a depth of at least 1 cm.
- (2) The thermometer must be tapped with the finger (or with a mechanical tapper) prior to each reading.

The accuracy of the temperature measurement, using a Beckmann thermometer under these conditions, is of the order of $\frac{1}{1000}^{\circ}$. With a good ordinary thermometer, graduated in tenths of a degree, the measurement of the depression should be accurate to between $\frac{1}{20}^{\circ}$ and $\frac{1}{50}^{\circ}$. For ordinary work, it is doubtful if the increased time occupied in making a freezing-point determination with a Beckmann thermometer is repaid by the gain in accuracy.

The Beckmann Thermometer.

The Beckmann thermometer (shown in Fig. 103) is usually graduated in hundredths of a degree, and can be read with a lens to $\frac{1}{10000}^{\circ}$. The scale, as a rule, covers only about 6° , but the thermometer may be used at any desired temperature by transferring mercury to or from the reservoir at the top.

On account of the permanent and semi-permanent alterations produced in the volume of the glass bulb if the thermometer is subjected to any large change in temperature, and since any one thermometer cannot be accurate at two widely different temperatures, separate thermometers must be reserved for freezing-point and for boiling-point experiments.

"Setting" a Beckmann Freezing-point Thermometer.

—If a Beckmann thermometer is to be used for freezing-point determinations with, say, benzene as solvent, the amount of

mercury in the bulb must be so adjusted that at 5.5° the top of the thread will lie somewhere on the upper half of the scale.

The thermometer bulb is placed in water, and heat is applied until the capillary is completely filled with mercury, and a small globule of mercury projects into the reservoir. The thermometer is then removed, inverted, and tapped gently until the mercury in the reservoir drops down and joins the thread. The thermometer is then cooled until the temperature (measured with an ordinary thermometer) is about 3° above the freezing-point of the solvent, *i.e.* for benzene it is cooled in water to about 8.5° . After keeping it for a few minutes at this temperature, the thermometer is removed from the water, and *at once* given a sharp downward jerk in order to break the thread of mercury at the bend above the reservoir. If there is difficulty in detaching the mercury in the reservoir, the thermometer should be held vertically with the bulb 3 to 4 inches above the palm of the left hand. The bulb is then brought down fairly sharply on the hand, the blow being delivered with the thermometer vertical throughout. Any side strain on the thermometer during this operation may break it.

The amount of mercury left in the bulb should be such that at 5.5° the top of the thread will lie on the upper half of the scale. A beaker of water is therefore cooled to 5.5° , using an ordinary thermometer to measure the temperature, and the Beckmann thermometer is placed in the water for a few minutes. If the top of the thread lies on the upper half of the scale, the thermometer is "set" for the experiment; if (at 5.5°) it is not on the scale or is on the lower portion, the above "setting" must be more carefully repeated.

"Setting" a Beckmann Boiling-point Thermometer.—

The procedure is identical with that described above, except that it is necessary so to set the thermometer that at the boiling-point of the pure solvent the top of the mercury thread comes on the lower half of the scale. The temperature of the bath used in the "setting" should therefore be about 8° above the boiling-point of the solvent to be used.

Determination of the Molar Weight of a Substance in Water, using a Beckmann Thermometer.

Having "set" the Beckmann thermometer, make sure that the top of the mercury thread lies on the upper half of the scale when the bulb is placed in melting ice, and, at the same time, note the reading on the thermometer to the nearest $\frac{1}{10}^{\circ}$. (This gives, very roughly, the freezing-point of the solvent and will be found useful later.) Once the thermometer has been set, it must be handled with care, in case the setting is disturbed.

Prepare the cooling-bath by adding a concentrated salt solution (about 20 per cent.) to crushed ice until the temperature falls to about -4° . Excess of ice must always be present. Add solid salt later if the temperature rises. Keep the bath well mixed and observe its temperature from time to time.

Measure 20 c.c. or 25 c.c. of water into the freezing-point tube. Place the tube directly in the cooling-bath and stir until the temperature falls to about 0.5° below the approximate freezing-point already noted. Add a nucleus of ice in order to induce crystallisation.¹ When the temperature begins to rise, quickly dry the tube and place it at once within the air-jacket. Stir steadily again and observe the temperature until it becomes constant, care being taken to tap the thermometer sharply with the finger before each observation is made.

In making further determinations of the freezing-point of the solvent or solution, the procedure is the same as that already described for benzene solutions, except that it is almost invariably necessary to add a nucleus of ice when the supercooling amounts to about 0.3° , in order to induce crystallisation.

¹ Mix some ice and salt in a beaker. By means of a glass rod (cooled in a test-tube placed in the same beaker) scrape off a minute quantity of the ice crystals that form *on the outside* of the beaker and bring the crystals into contact with the lower end of the stirrer which is raised to the level of the side-tube for that purpose.

BECKMANN'S BOILING-POINT METHOD.

The boiling-point of a solution is always higher than that of the pure solvent, and, with dilute solutions, the elevation of the boiling-point is proportional to the concentration of the dissolved substance.

If s grams of a substance of molar weight M are dissolved in w grams of a solvent, and if the elevation of the boiling-point is e° , the molar weight of the substance may be found from the formula,

$$M = K \frac{s}{e w}$$

where K is a constant depending on the nature of the solvent. K is one thousand times the elevation of the boiling-point that would be observed with a solution containing 1 mole of a substance dissolved in 1000 grams of the solvent. The constants for the commonest solvents are given in the following table:—

<i>Solvent</i>	<i>Boiling-point</i>	<i>K</i>
Acetone	56.1°	1710
Benzene	80.1°	2650
Chloroform	61.2°	3660
Ethyl acetate	77.2°	2680
Ethyl alcohol	78.4°	1150
Ethyl ether	34.6°	2100
Methyl alcohol	64.7°	860
Water	100.0°	520

It is usually more convenient to use a known *volume* of the solvent instead of a known *weight*. The molar weight can then be calculated from the formula,

$$M = k \frac{s}{e v}$$

where v is the volume in cubic centimetres at 15° of the solvent. The values for k are as follows:—

	<i>k</i>		<i>k</i>
Acetone	2150	Ethyl alcohol	1450
Benzene	3000	Ethyl ether	2920
Chloroform	2430	Methyl alcohol	1080
Ethyl acetate	2930	Water	520

The method cannot be used if the dissolved substance is appreciably volatile at the boiling-point of the solvent. In general, the boiling-point of the solute must be at least 120° above that of the solvent.

The Apparatus (Fig. 105) consists essentially of a boiling-tube with two side-tubes, one of which, S, is provided with a glass stopper. Inside the longer side-tube T is fitted a small condenser C. If the solvent is hygroscopic, a calcium chloride tube is attached to the air inlet R. The boiling-tube stands on an asbestos card, so that the end of the tube closes a circular hole in the asbestos, but does not touch a sheet of wire gauze placed beneath the asbestos.

The boiling-tube is protected from air-draughts by means of a glass cylinder G, which is covered by a sheet of mica M. The sheet of mica is perforated by a hole which is just large enough to admit the boiling-tube.

A thermometer that can be read to at least hundredths of a degree is also required — a Beckmann thermometer which can be read to $\frac{1}{500}^{\circ}$ or $\frac{1}{1000}^{\circ}$ is usually employed.

Procedure.—Clean and dry the boiling-point tube. Suspend it by means of a fine wire from the hook of the balance, and weigh the tube and wire. Add 10 to 12 c.c. of the solvent and weigh again. (The weighing of the

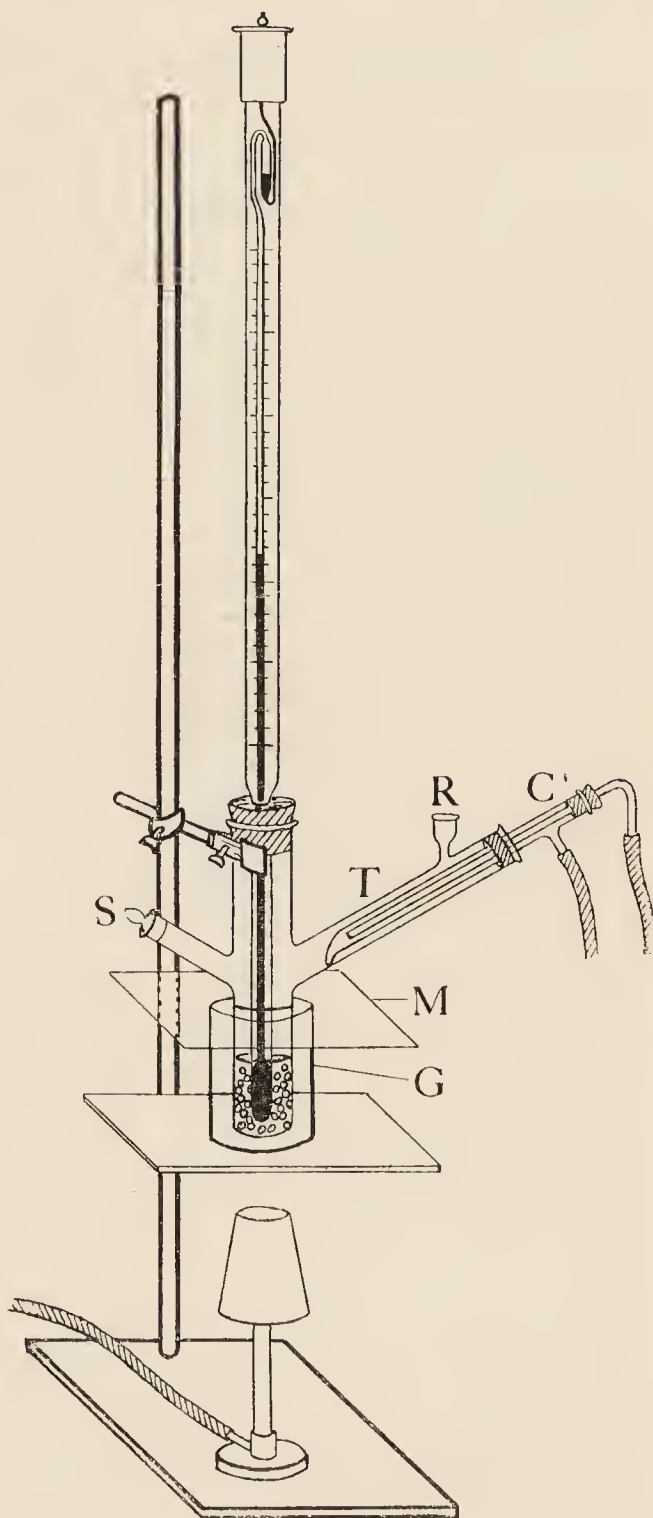


FIG. 105.

somewhat awkward piece of apparatus may be avoided by taking a measured volume of solvent, and using in the calculation of results the "volume constants" given on p. 406.)

Arrange the apparatus as shown in Fig. 105, in a place where it will not be exposed to draughts. The bottom of the thermometer should be at least 1 cm. from the bottom of the boiling-point tube. If a Beckmann thermometer is used, it must be "set" for the desired temperature as described on p. 404. Through the side-tube add some clean, dry garnets (platinum tetrahedra are better) until the thermometer bulb is completely surrounded by them. Heat the liquid by means of a small flame until it boils so briskly that there is plentiful condensation on the condenser C, which is kept cool by means of a current of water. The point of the condenser should be so close to the wall of the side-tube that the condensed liquid runs back steadily without collecting into drops. (If drops form, they cause fluctuations in the temperature through irregular cooling of the boiling liquid.)

About twenty minutes after the liquid begins to boil, the temperature should become constant. The variation of temperature in the course of five minutes should not exceed 0.01° . If it does not become constant in about this time, there is some fault in the arrangement of the apparatus, or the heating is not properly adjusted. (It is a common mistake to boil too gently.) Examine the apparatus to be sure that the flame gases cannot enter the air-mantle, and attend to the other points specified above.

When the boiling-point of the pure solvent has been ascertained, remove the flame until ebullition ceases. Introduce a weighed portion (*cf.* p. 401) of the substance, preferably in the form of a tablet, through the side-tube S, and boil again until the temperature becomes constant. Note the boiling-point of the solution. Add further portions of the substance, determine the boiling-point after each addition, and from each set of data calculate the molar weight. The amount added should be such that the boiling-point is raised about 0.3° by each addition of substance.

Modification of Beckmann's Method with Electrical Heating.

Many of the practical difficulties met with in the ordinary boiling-point method may be avoided by using as a source of heat a platinum wire spiral immersed in the liquid and heated by means of an electric current. Very steady boiling-points are obtained in this way.

The boiling-point tube used is the same as that already described. It is placed in a Dewar vacuum vessel, or in a tall bottle—the space between the bottle and tube being packed with cotton wool (Fig. 106).

Through the cork of the boiling-tube are passed two stout nickel (or platinum) wires, which are connected at the lower ends by a spiral of fine platinum wire (about 0.1 mm. in diameter). Nickel wires are not always admissible, and there may be substituted two glass tubes (about 4 mm. in diameter) with short pieces of fairly stout platinum wire sealed into the closed lower ends. The resistance spiral is attached to these platinum wires, and electrical connection with the spiral is made by placing a little mercury in the tubes and dipping amalgamated copper wires into the mercury. The resistance spiral should be freshly platinised.

The current necessary for boiling the liquid is provided by a battery of four or five accumulators. The amount of current required varies with the nature of the solvent and the resistance of the heating spiral, and must be adjusted by means of a rheostat and ammeter placed in the circuit. As a rule a current of from 1.5 to 3 amperes is required, and as the observed boiling-point depends to some extent on the heat supplied (*i.e.* on the amount of current), it is advisable to keep the current constant throughout each set of experiments. The thermometer bulb should be at least 2 cm. above the heating spiral.

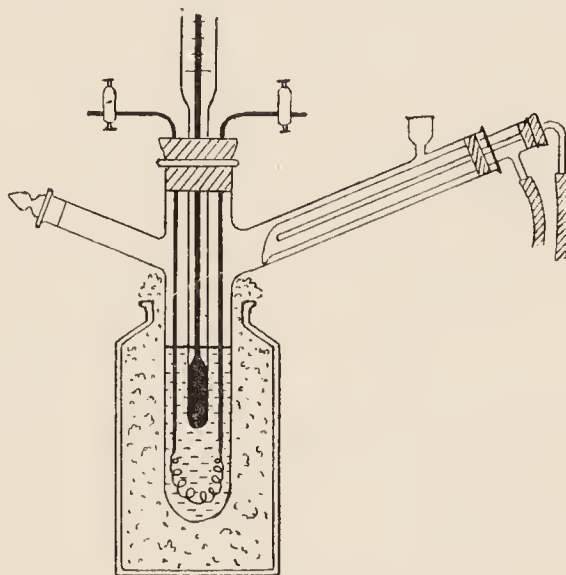


FIG. 106.

LANDSBERGER'S BOILING-POINT METHOD.*(Walker-Lumsden Modification.)*

By passing the vapour of the boiling solvent through a solution, the latter becomes heated to the boiling-point—but not above it, since the vapour that heats the solution is originally at a lower temperature than the boiling solution itself. Superheating is thus practically impossible, and real equilibrium between the solution and the vapour of the solvent is attained. This method of heating is used in Landsberger's apparatus. For ordinary purposes, where an accuracy of about 5 per cent. in the determination of a molar weight is sufficient, the following modification of the method is more expeditious and convenient than either the Beckmann or the original Landsberger method.

In this method, a series of measurements at different concentrations can be made with a single weighed portion of the substance. The boiling-tube is graduated, and the quantity of liquid is found by noting its volume at the boiling-point. The molar weight is calculated in the usual manner, but the molar elevation constant for each solvent is one thousand times the elevation of the boiling-point that would be produced if 1 mole of a substance were contained in 1000 c.c. of the solution at its boiling-point. The formula is

$$M = k \frac{s}{e v}$$

where e is the elevation of the boiling-point, s the weight of substance, and v the volume in cubic centimetres of the solution at its boiling-point. The values of the constant k for the commonest solvents are given in the following table:—

<i>Solvent</i>	<i>Boiling-point</i>	<i>k</i>
Acetone	56.1°	2220
Benzene	80.1°	3280
Chloroform	61.2°	2600
Ethyl alcohol	78.4°	1560
Ethyl ether	34.6°	3030
Methyl alcohol	64.7°	1150
Water	100.0°	540

The best solvents to use are acetone, methyl alcohol, ethyl

alcohol, and ether. The boiling-point of the solute must be at least 150° above that of the solvent.

The Apparatus required is shown in Fig. 107. The lower portion of the boiling-tube B is graduated (usually up to 30 c.c.). The tube is expanded into a bulb above the

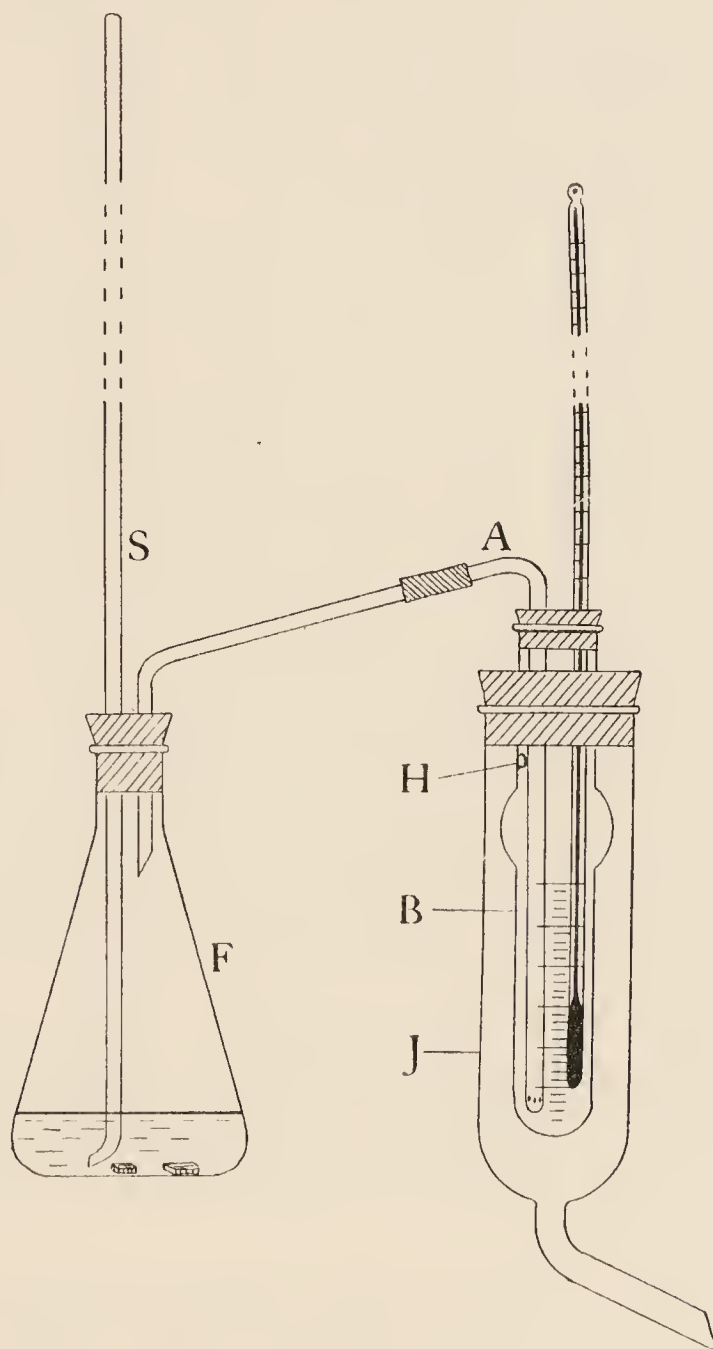


FIG. 107.

graduations, and is pierced by a small hole at H. It is fitted with a cork which carries the thermometer (graduated in tenths of a degree) and a tube A which leads from a conical flask F. The tube A is sealed at the lower end and perforated by a ring of fine holes as near the end as possible. The boiling-tube is completely surrounded by the glass jacket J, and the jacket terminates below in a narrow tube

which is connected with a condenser when a volatile solvent, such as ether, is in use. With less volatile solvents, a flask, placed in cold water, may be substituted for the condenser. The flask F in which the solvent is boiled is provided with a safety tube S, which should be at least 2 feet long.

Procedure.—Clean, dry, and arrange the apparatus as shown in the diagram. The inlet-tube should reach almost to the bottom of the boiling-tube, and the fine holes at the end of it must be at a lower level than the bulb of the thermometer. Introduce about 10 c.c. of the pure solvent into the boiling-tube B and about 150 c.c. of it into the flask F, which is supported over a wire gauze. In order to ensure regular ebullition, place a few pieces of porous tile in the flask F, and boil the liquid briskly, so that the vapour passes steadily through the tube A into the graduated tube B. At first it will all be condensed, but, when the liquid in B becomes hot, some of the vapour will pass through it and, escaping through the hole H into the outer jacket, will condense and collect in the flask below. The liquid in B is thus gradually heated to its boiling-point, and the temperature becomes constant at this point. When the temperature is constant, read the thermometer as accurately as possible with the aid of a lens. This gives the boiling-point of the pure solvent.

The liquid in B is now returned to the flask F in the following manner:—Remove the flame and at the same time close the top of the safety tube S by pressing a finger on it. As the flask cools, almost the whole of the liquid will be drawn back into it.

Withdraw the cork from the graduated tube and add a weighed amount (about 1 gram) of the substance. Place another piece of porous tile in the flask and boil again. When the condensed vapour is again dropping into the receiver, and when the volume of liquid in the graduated tube has reached 10 to 12 c.c., note the temperature accurately, and then *at once extinguish the flame and disconnect the flask F from the graduated boiling-tube*. Ascertain the volume of the solution as follows:—Remove the cork from the graduated tube, lift the thermometer and inlet-tube out of the liquid, and read the volume as accurately as

possible. In this way, the boiling-point and the corresponding concentration of the solution are obtained.

Fit the apparatus together again, add another piece of porous tile, and again boil the liquid in the flask. The temperature falls at first but soon rises once more, reaches a maximum, and then begins to fall again slowly and steadily on account of the progressive dilution of the solution. When this stage is reached, again read the boiling-point and the corresponding volume of the solution. Continue this series of operations until the volume has reached 20 to 25 c.c., and several sets of boiling-point observations have been obtained. From each set of data calculate the molar weight.

Notes.—The amount of dissolved substance should be sufficient to give an elevation of the boiling-point of from 1° — 2° when the volume of the solution is 10—12 c.c.

A fresh piece of porous tile must be placed in the flask *each* time the boiling is interrupted.

Vigorous boiling is necessary. The condensed liquid should collect in the receiver at the rate of about two drops per second. (With ether as solvent, a condenser *must* be inserted below the jacket.)

Most of the solvents employed for this method are inflammable; care must be taken, therefore, to extinguish the flame or to remove it to at least 3 feet from the apparatus before withdrawing a cork.

Quick working, especially in measuring the volume after noting the temperature, is essential to success with this method.

APPENDIX

LIST OF COMMON REAGENTS.

Unless the contrary is stated, it is to be understood that any reagent mentioned in the text has the composition and concentration indicated below. The concentrations, etc., are those adopted in the Chemistry Department, University of Edinburgh. For convenience, the quantity necessary for the preparation of a Winchester of solution is given in each case. A Winchester contains about 2500 c.c.

For quantitative work it is usually necessary to prepare solutions as required, since the bench solutions, even when prepared from the purest chemicals, usually contain appreciable amounts of impurities dissolved from the glass.

Acids and Alkalis.

The dilute acids and alkalis are 2N, with the exception of dilute sulphuric acid, barium hydroxide, and calcium hydroxide.

Concentrated Sulphuric Acid (Density 1.84) is approximately 36N. It often contains traces of lead, iron, and nitric acid.

Dilute Sulphuric Acid (approximately 4N) is prepared by diluting 270 c.c. of the concentrated acid to a Winchester.

Concentrated Nitric Acid (Density 1.42).—This is the constant boiling-point acid and contains about 68 per cent. of nitric acid. It is about 16N. The commonest impurities are chloride and sulphate.

Dilute Nitric Acid (approximately 2N) is prepared by diluting 300 c.c. of the concentrated acid to a Winchester.

Concentrated Hydrochloric Acid (Density 1.16) is about 10N. It often contains traces of iron, arsenic, and sulphate.

Dilute Hydrochloric Acid (approximately 2N) is prepared by diluting 500 c.c. of the concentrated acid to a Winchester.

Acetic Acid (approximately 2N) is prepared by diluting 280 c.c. of glacial acetic acid (about 17N) to a Winchester.

Sodium Hydroxide (approximately 2N) is prepared by dissolving 200 grams of sodium hydroxide ("white sticks") in a Winchester. It always contains carbonate, and may also contain chloride, sulphate, alumina, and silica.

Concentrated Ammonia (Density 0.88) is about 18N. The commonest impurities are carbonate, silicate, and aluminate (derived from glass bottles), and tarry matter.

Dilute Ammonia (approximately 2N) is prepared by diluting 250 c.c. of concentrated ammonia to a Winchester.

Ammonium Carbonate (approximately 2N) is prepared by dissolving 200 grams of commercial ammonium carbonate (sesqui-carbonate), together with 100 c.c. of 0.880 ammonia, in a Winchester.

Sodium Carbonate (approximately 2N) is prepared by dissolving 250 grams of the anhydrous salt, or 680 grams of the decahydrate ($\text{Na}_2\text{CO}_3, 10 \text{H}_2\text{O}$) in a Winchester. It usually contains traces of chloride and sulphate, and some samples are worthless on account of the amount of these impurities. It occasionally contains traces of ammonia.

Calcium Hydroxide (approximately 0.04N) is a saturated solution prepared from pure lime.

Barium Hydroxide (approximately 0.4N) is a saturated solution of barium hydroxide in water.

Other Common Reagents.

Alcohol.—Rectified spirit contains 93 to 95 per cent. of ethyl alcohol. The "66 over-proof" spirit contains 93 per cent. of alcohol.

Ammonium Chloride (approximately 2N) contains 260 grams of the salt, NH_4Cl , in a Winchester.

Ammonium Oxalate (approximately 0.5N) contains 85 grams of the salt, $(\text{COONH}_4)_2, \text{H}_2\text{O}$, in a Winchester.

Ammonium Phosphate (approximately 0.5N) contains 55 grams of the salt, $(\text{NH}_4)_2\text{HPO}_4$, in a Winchester.

Ammonium Sulphide (approximately 2N) is prepared by saturating 1200 c.c. of 2N ammonia with hydrogen sulphide, and then adding an equal volume of 2N ammonia.

Barium Chloride (approximately 0.5N) contains 145 grams of the salt, $\text{BaCl}_2, 2\text{H}_2\text{O}$, in a Winchester.

Barium Nitrate (approximately 0.5N) contains 150 grams of the salt $\text{Ba}(\text{NO}_3)_2$, in a Winchester.

Bromine Water (approximately 0.5N) is a saturated solution. It usually contains chlorine and iodine as impurities.

Calcium Nitrate (approximately 0.5N) contains 150 grams of the salt, $\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}$, in a Winchester.

Calcium Sulphate (approximately 0.03N) is a saturated solution.

Copper Nitrate (approximately 0.2N) contains 70 grams of the salt, $\text{Cu}(\text{NO}_3)_2, 6\text{H}_2\text{O}$, in a Winchester.

Ferrous Sulphate (approximately N) is prepared by dissolving 335 grams of the salt, $\text{FeSO}_4, 7\text{H}_2\text{O}$, together with 300 c.c. of dilute sulphuric acid, in a Winchester.

Ferric Chloride (approximately 0.2N) is prepared by dissolving 45 grams of the salt, $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$, in 50 c.c. of concentrated hydrochloric acid and diluting to a Winchester.

Lead Acetate (approximately 0.5N) is prepared by dissolving 220 grams of the salt, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$, together with 30 c.c. of glacial acetic acid, in a Winchester.

Mercuric Chloride (approximately 0.2N) contains 65 grams of the salt, HgCl_2 , in a Winchester.

Potassium Ferrocyanide (approximately 0.2N) contains 50 grams of the salt, $\text{K}_4\text{Fe}(\text{CN})_6, 3\text{H}_2\text{O}$, in a Winchester.

Potassium Chromate (approximately 0.2N) contains 50 grams of the salt, K_2CrO_4 , in a Winchester.

Potassium Iodide (approximately 0.1N) contains 40 grams of the salt, KI , in a Winchester.

Sodium Acetate (approximately N) contains 325 grams of the salt, $\text{NaC}_2\text{H}_3\text{O}_2, 3\text{H}_2\text{O}$, in a Winchester.

Stannous Chloride (approximately 0.2N) is made by dissolving 60 grams of the salt, $\text{SnCl}_2, 2\text{H}_2\text{O}$, in 250 c.c. of concentrated hydrochloric acid and diluting to a Winchester. A piece of tin placed in each bottle preserves the salt in the stannous state.

Silver Nitrate (approximately 0.1N) contains 40 grams of the salt, AgNO_3 , in a Winchester.

SPECIAL REAGENTS.

Magnesia Mixture.—Dissolve 70 grams of ammonium chloride and 60 grams of magnesium chloride in water, add 100 c.c. of concentrated ammonia, and dilute to 1 litre. Filter a day or two after preparation.

“Cupferron.”—In a wide-mouthed bottle or jar place 1 litre of water, 63 grams of nitrobenzene (freshly distilled), and 30 grams of ammonium chloride. Stir the mixture vigorously, by means of an efficient stirring apparatus, so as to form a milky emulsion. (The stirring must be so vigorous that no nitrobenzene settles out of the emulsion.) To the emulsion add 84 grams of zinc dust in small portions at one time. (With zinc dust containing less than 80 per cent. of zinc, a proportionately larger quantity must be used.) Allow the temperature of the mixture to rise to 50° , but prevent it rising higher by adding small pieces of ice from time to time. After all the zinc dust has been added (this takes about twenty minutes), continue stirring until the temperature has fallen from 5° — 8° below the maximum. Filter the warm mixture through a Büchner funnel, and wash the zinc hydroxide with about 150 c.c. of warm water. Cool the filtrate in ice and filter off the phenylhydroxylamine that separates. Saturate the filtrate with common salt, cool in ice, and filter again with suction. The yield of moist phenylhydroxylamine is about 70 per cent. of the theoretical amount. It must be converted *without delay* into the nitroso-derivative.

[As phenylhydroxylamine solutions are vigorous skin poisons, the

hands should be washed with water and alcohol, in case they have come into contact with such solutions.]

Weigh the moist phenylhydroxylamine and dissolve it in about 300 c.c. of ether. Filter the solution through a dry paper. (The insoluble residue—chiefly salt—may be weighed in order to ascertain the amount of actual phenylhydroxylamine present.) Cool the solution to 0° in ice and salt, and pass a rapid current of dry ammonia gas into it. After about ten minutes, add slowly from a dropping funnel the theoretical quantity of freshly distilled amyl nitrite (107 grams for every 100 grams of phenylhydroxylamine). Maintain the current of ammonia gas and keep the temperature below 10° . (The temperature may be readily controlled by adding the amyl nitrite at an appropriate rate.) After the amyl nitrite has been added, stir the mixture for about ten minutes. Filter, wash the cupferron several times with ether, and dry it by spreading it on filter paper. Preserve the cupferron in a bottle with a lump of ammonium carbonate held between the inner surface of the cork and a piece of filter paper.

Hydrochloroplatinic Acid.—This is usually obtained as the hydrate $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, which contains 37.66 per cent. of platinum. In order to prepare a solution containing 10 per cent. of platinum (10 grams of platinum per 100 c.c. of solution), dissolve 1 oz. of this hydrate in about 50 c.c. of water, filter, and wash the vessel and the filter two or three times with water. Dilute the filtrate and washings to 106 c.c.

The preparation of this “10 per cent.” solution from commercial platinum is described in Treadwell’s *Analytical Chemistry*, vol. i.

Indicator Solutions.

Litmus.—Dissolve 1 gram of azolitmin in 1 litre of water.

Methyl Orange.—Dissolve 0.05 gram of the solid in 1 litre of water.

Methyl Red.—Dissolve 0.05 gram of the solid in 800 c.c. of alcohol, and dilute to 1 litre with water.

Phenolphthalein.—Dissolve 1 gram of the solid in 500 c.c. of alcohol, and dilute to 1 litre with water.

STANDARD SOLUTIONS FOR ANALYSIS.

It is customary for beginners to perform their first quantitative exercises with pure salts of known composition. There are many objections to this system—the most serious is that the exercise does not imitate the conditions met with in ordinary practice. For example, when working with a known quantity of material, the problem of how much precipitant to add does not, as a rule, present any difficulty; in this important particular, therefore, the exercise lacks much of the educational value it should possess. For this reason alone, it is desirable that all quantitative exercises should be performed with solids or solutions of “unknown” composition.

The most convenient system whereby a number of students can be

provided with different exercises is to use standard solutions, and the following list may be found serviceable. All the solutions mentioned below can be prepared by weight from substances that are obtainable commercially in a pure state. The quantities given are the amounts required for the preparation of 1 litre of solution. With these concentrations, 20 to 30 c.c. is a suitable quantity for an analysis. For small classes, the portions for analysis may be measured with a pipette or burette; for larger classes, it is an advantage to store the solution in a bottle with a burette permanently attached, as shown in Fig. 28, on p. 64.

Aluminium	. 70 grams of ammonia alum, $\text{Al}(\text{NH}_4)(\text{SO}_4)_2, 12\text{H}_2\text{O}$.
Ammonia	. 40 grams of dry ammonium chloride, NH_4Cl .
Arsenic	. 6 grams of arsenious oxide, As_2O_3 , dissolved in dilute hydrochloric acid.
Barium	. 20 grams of barium chloride, $\text{BaCl}_2, 2\text{H}_2\text{O}$.
Bromide	. 15 grams of dry potassium bromide, KBr .
Calcium	. 20 grams of pure calcspar, CaCO_3 , dissolved in dilute hydrochloric acid.
Carbonate	. 100 grams of uneffloresced crystals of sodium carbonate, $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$.
Chloride	. 20 grams of barium chloride, $\text{BaCl}_2, 2\text{H}_2\text{O}$.
Chromate	. 20 grams of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
Copper	. 30 grams of copper sulphate, $\text{CuSO}_4, 5\text{H}_2\text{O}$.
Iodide	. 20 grams of dry potassium iodide, KI .
Iron	. 50 grams of ferric alum, $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2, 12\text{H}_2\text{O}$.
Lead	. 20 grams of dry lead nitrate, $\text{Pb}(\text{NO}_3)_2$. It is advisable to recrystallise this salt from a dilute nitric acid solution.
Magnesium	. 25 grams of magnesium sulphate, $\text{MgSO}_4, 7\text{H}_2\text{O}$.
Manganese	. Dissolve 20 grams of pure potassium permanganate in water, and pass sulphur dioxide until it is completely decolorised and the precipitated manganese dioxide has dissolved. Boil until free from sulphur dioxide, and dilute to 1 litre.
Mercury	. 10 grams of red mercuric oxide, HgO , dissolved in concentrated nitric acid, boiled, and diluted to 1 litre.
Nickel	. 70 grams of nickel ammonium sulphate, $\text{NiSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$.
Nitrate	. 100 grams (for reduction method) or 2.5 grams (for oxidation method) of dry potassium nitrate, KNO_3 .
Phosphate	. 0.8 gram of dry potassium phosphate, KH_2PO_4 (for the molybdate method).
Potassium	. 15 grams of dry potassium chloride, KCl .
Silver	. 20 grams of dry silver nitrate, AgNO_3 .
Sulphate	. 25 grams of magnesium sulphate, $\text{MgSO}_4, 7\text{H}_2\text{O}$.
Zinc	. 30 grams of zinc sulphate, $\text{ZnSO}_4, 7\text{H}_2\text{O}$.

TYPICAL ANALYSES.

Various Glasses.

	SiO ₂ .	PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	Total.
Table glass .	70·61	0·70	4·92	11·95	12·28	100·46
Table glass .	70·04	...	1·81	...	1·27	13·11	13·98	100·21
Plate glass .	71·72	...	1·29	0·13	15·54	11·49	...	100·17
Mirror glass .	77·35	1·25	15·05	6·33	99·98
White bottle glass* .	68·64	...	2·83	0·71	14·94	13·01	...	100·37
Flint glass .	42·65	43·17	0·28	...	0·28	...	13·89	100·27

* Contained also 0·24 per cent. of MnO. (Traces of Mn are almost invariably present in colourless glasses.)

Various Silicates.

	SiO ₂ .	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
Albite .	68·80	...	19·43	...	0·20	nil	11·68	...	100·11
Albite .	67·99	...	19·23	...	1·84	1·25	9·69	...	100·00
Albite .	68·40	...	19·89	0·90	10·69	...	99·88
Orthoclase	66·56	...	19·18	...	0·52	6·94	6·56	...	99·76
Orthoclase	66·58	...	21·26	...	1·18	0·76	10·26	0·16	100·20
A clay .	63·69	...	17·02	10·18	0·97	...	4·02	4·05	99·93
Talc .	63·42	31·49	...	0·57	4·38	99·86
Talc .	62·78	31·16	...	1·85	4·32	100·11

Iron Pyrites.

S.	Cu.	Fe.	Mn.	Zn.	Insoluble residue.	Total.
43·03	2·50	39·54	0·06	0·42	14·68	100·23
42·59	1·49	40·11	0·03	0·72	15·01	99·95
53·37	2·39	44·47	100·23
52·71	0·24	44·23	2·58	99·76
48·73	...	42·94	...	0·18	7·82	99·67

Dolomite.

CaO.	MgO.	CO ₂ .	Fe ₂ O ₃ + Al ₂ O ₃ .	FeO.	H ₂ O.	Insoluble residue.	Total.
29·51	20·29	47·22	0·82	...	1·05	1·33	100·22
30·75	25·18	42·01	...	0·83	0·07	1·30	100·14
29·61	12·94	44·72	...	12·99	100·26

Cassiterite.

SnO ₂ .	Fe ₂ O ₃ .	CaO.	SiO ₂ .	Total.
98·74	0·12	0·41	0·19	99·46

Cassiterite often contains traces of As and Zn.

Garnet (Pyrope).

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	H ₂ O.	Total.
40·92	22·45	5·46	8·11	0·46	17·85	5·04	0·10	100·39

Traces of Cr are usually found in garnets.

Manganese Minerals.

	MnO ₂ .	MnO.	Fe ₂ O ₃ .	BaO.	H ₂ O.	Insoluble residue.	Total.
Pyrolusite. .	86·45	6·02	0·93	1·31	1·22	4·11	100·04
Pyrolusite. .	69·06	18·16	0·55	...
Manganite .	48·47	42·03	7·41	1·72	99·63

Zinc Blende.

S.	Zn.	Cd.	Fe.	Mn.	Pb.	Total.
32·98	64·92	1·05	0·57	0·37	0·15	100·04
33·25	50·02	0·30	15·44	nil	1·01	100·02

Copper Pyrites.

S.	Fe.	Cu.	Ag.	Pb.	Insoluble residue.	Total.
30·50	21·08	48·40	trace	99·98
33·18	32·65	32·79	nil	0·35	1·04	100·01
36·15	29·34	32·25	nil	0·30	2·09	100·13

Density and Concentration of Hydrochloric Acid at 15°.
(Normal HCl = 36·47 grams per litre.)

Density 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Nor- mality.	Density 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Nor- mality.
1·010	2·14	22	0·6	1·110	21·9	243	6·7
1·020	4·13	42	1·2	1·120	23·8	267	7·3
1·030	6·15	64	1·8	1·130	25·7	291	8·0
1·040	8·16	85	2·3	1·140	27·7	315	8·6
1·050	10·17	107	2·9	1·150	29·6	340	9·3
1·060	12·19	129	3·5	1·160	31·5	366	10·0
1·070	14·17	152	4·2	1·170	33·5	392	10·8
1·080	16·15	174	4·8	1·180	35·4	418	11·7
1·090	18·1	197	5·4	1·190	37·2	443	12·1
1·100	20·0	220	6·0	1·200	39·1	469	12·9

Density and Concentration of Sulphuric Acid at 15°.
(Normal H₂SO₄ = 49·04 grams per litre.)

Density 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Nor- mality.	Density 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Nor- mality.
1·006	1	10·1	0·20	1·449	55	797	16·25
1·013	2	20·3	0·41	1·502	60	901	18·38
1·020	3	30·4	0·62	1·558	65	1013	20·65
1·026	4	41·0	0·84	1·615	70	1130	23·05
1·033	5	51·6	1·05	1·674	75	1248	25·60
1·040	6	62·4	1·27	1·732	80	1386	28·26
1·047	7	73·3	1·49	1·784	85	1520	30·92
1·054	8	84·3	1·72	1·820	90	1640	33·40
1·061	9	95·5	1·95	1·825	91	1660	33·86
1·068	10	106·8	2·18	1·829	92	1680	34·32
1·104	15	160·6	3·38	1·833	93	1710	34·76
1·142	20	228	4·66	1·836	94	1730	35·20
1·182	25	296	6·02	1·839	95	1750	35·62
1·222	30	367	7·48	1·841	96	1770	36·03
1·264	35	444	9·02	1·841	97	1790	36·42
1·306	40	522	10·66	1·841	98	1800	36·79
1·351	45	608	12·40	1·839	99	1820	37·13
1·399	50	700	14·26	(1·836)	100	(1836)	(37·4)

Density and Concentration of Nitric Acid at 15°.*(Normal HNO₃ = 63.02 grams per litre.)*

Density 15°/4°.	100 grams contain grams HNO ₃ .	1 litre contains grams HNO ₃ .	Nor- mality.	Density 15°/4°.	100 grams contain grams HNO ₃ .	1 litre contains grams HNO ₃ .	Nor- mality.
1.010	1.90	19	0.30	1.280	44.41	568	9.01
1.020	3.70	38	0.60	1.300	47.49	617	9.8
1.040	7.26	75	1.19	1.320	50.71	669	10.6
1.060	10.68	113	1.79	1.340	54.07	725	11.5
1.080	13.95	151	2.35	1.360	57.57	783	12.4
1.100	17.11	188	2.99	1.380	61.27	846	13.4
1.120	20.23	227	3.60	1.400	65.30	914	14.5
1.140	23.31	266	4.22	1.420	69.80	991	15.7
1.160	26.36	306	4.84	1.440	74.68	1075	17.1
1.180	29.38	347	5.51	1.460	79.98	1168	18.5
1.200	32.36	388	6.16	1.480	86.05	1274	20.2
1.220	35.28	430	6.83	1.500	94.1	1410	22.4
1.240	38.29	475	7.54	1.510	98.1	1480	23.5
1.260	41.34	521	8.25	1.520	99.7	1515	24.0

Density and Concentration of Perchloric Acid at 15°.

Density 15°/4°.	100 grams contain grams HClO ₄ .	1 litre contains grams HClO ₄ .	Density 15°/4°.	100 grams contain grams HClO ₄ .	1 litre contains grams HClO ₄ .
1.030	5.25	54	1.240	33.85	420
1.060	10.06	107	1.270	37.08	471
1.090	14.56	159	1.300	40.10	521
1.120	18.88	212	1.360	45.71	622
1.150	22.99	264	1.420	50.91	723
1.180	26.82	316	1.540	60.04	925
1.210	30.45	369	1.675	70.15	1175

**Density and Concentration
of Potassium Hydroxide
at 15°.**

Density 15°/4°.	100 grams contain grams KOH.	1 litre contains grams KOH.
1·083	5	52
1·082	10	108
1·134	15	178
1·176	20	235
1·230	25	307
1·287	30	386
1·346	35	471
1·411	40	564
1·473	45	663
1·538	50	769

**Density and Concentration
of Sodium Hydroxide at
15°.**

Density 15°/4°.	100 grams contain grams NaOH.	1 litre contains grams NaOH.
1·058	5	53
1·113	10	111
1·170	15	175
1·224	20	245
1·279	25	320
1·332	30	400
1·383	35	484
1·433	40	573
1·481	45	666
1·529	50	765

Density and Concentration of Ammonia Solutions at 15°.

(Normal NH_3 = 17·03 grams per litre.)

Density 15°/4°.	100 grams contain grams NH_3 .	1 litre contains grams NH_3 .	Nor- mality.	Density 15°/4°.	100 grams contain grams NH_3 .	1 litre contains grams NH_3 .	Nor- mality.
0·990	2·31	22·9	1·3	0·980	18·64	173·4	10·2
0·980	4·80	47·0	2·8	0·920	21·75	210·1	11·8
0·970	7·31	70·9	4·2	0·910	24·99	227·4	13·4
0·960	9·91	95·1	5·6	0·900	28·33	255·0	15·0
0·950	12·74	121·0	7·1	0·890	31·75	282·6	16·6
0·940	15·63	146·9	8·6	0·880	35·70	314·2	18·5

Density of Aqueous Alcohol at 15°.

Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.	Density 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.
0·983	10	98	0·872	70	610
0·971	20	194	0·860	75	645
0·957	30	287	0·848	80	678
0·939	40	376	0·835	85	710
0·918	50	459	0·822	90	740
0·895	60	537	0·808	95	768
0·884	65	574	0·793	100	793

Weight of 1 Litre of Various Dry Gases at 0° and 760 mm.

	Grams.		Grams.
Air	1·2928	Methane	0·7160
Carbon monoxide . .	1·2506	Nitric oxide . . .	1·3412
Carbon dioxide . . .	1·9652	Nitrogen	1·2505
Hydrogen	0·0900	Oxygen	1·4292

Vapour Pressure of Water.

Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.
	mm.		mm.		mm.
4°	6·1	14°	11·9	24°	22·2
5°	6·5	15°	12·7	25°	23·5
6°	7·0	16°	13·6	26°	25·0
7°	7·5	17°	14·4	27°	26·5
8°	8·0	18°	15·4	28°	28·1
9°	8·6	19°	16·4	29°	29·8
10°	9·2	20°	17·4	30°	31·5
11°	9·8	21°	18·5	31°	33·4
12°	10·5	22°	19·7	32°	35·4
13°	11·2	23°	20·9	33°	37·4

Vapour Pressure of Potassium Hydroxide Solutions.

Temperature.	Vapour pressure of 40 per cent. solution.	Vapour pressure of 50 per cent. solution.
	mm.	mm.
10°	6·5	5·6
12°	7·5	6·5
14°	8·4	7·3
16°	9·6	8·3
18°	10·9	9·5
20°	12·4	10·8
22°	13·9	12·1

The “40 per cent.” solution is one containing 40 grams of potassium hydroxide per 100 grams of water, and the “50 per cent.” solution one containing 50 grams of potassium hydroxide per 100 grams of water.

Logarithms.

	0	1	2	3	4	5	6	7	8	9									
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039									
101	0043	0048	0052	0056	0060	0065	0069	0073	0077	0082									
102	0086	0090	0095	0099	0103	0107	0111	0116	0120	0124									
103	0128	0133	0137	0141	0145	0149	0154	0158	0162	0166									
104	0170	0175	0179	0183	0187	0191	0195	0199	0204	0208									
105	0212	0216	0220	0224	0228	0233	0237	0241	0245	0249									
106	0253	0257	0261	0265	0269	0273	0278	0282	0286	0290									
107	0294	0298	0302	0306	0310	0314	0318	0322	0326	0330									
108	0334	0338	0342	0346	0350	0354	0358	0362	0366	0370									
109	0374	0378	0382	0386	0390	0394	0398	0402	0406	0410	1	2	3	4	5	6	7	8	9
110	0414	0418	0422	0426	0430	0434	0438	0441	0445	0449									
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

Logarithms.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Atomic Weights.

Aluminium	Al	27·0	Mercury	Hg	200·6
Antimony	Sb	121·8	Molybdenum	Mo	96·0
Argon	A	39·9	Neodymium	Nd	144·3
Arsenic	As	75·0	Neon	Ne	20·2
Barium	Ba	137·4	Nickel	Ni	58·7
Bismuth	Bi	209·0	Nitrogen	N	14·008
Boron	B	10·8	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·000
Cadmium	Cd	112·4	Palladium	Pd	106·7
Cæsium	Cs	132·8	Phosphorus	P	31·0
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·2	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·1
Chromium	Cr	52·0	Radon	Rn	222·1
Cobalt	Co	58·9	Rhodium	Rh	102·9
Columbium	Cb	93·2	Rubidium	Rb	85·4
Copper	Cu	63·57	Ruthenium	Ru	101·7
Dysprosium	Dy	162·5	Samarium	Sa	150·4
Erbium	Er	167·4	Scandium	Sc	45·1
Europium	Eu	152	Selenium	Se	79·2
Fluorine	F	19·0	Silicon	Si	28·1
Gadolinium	Gd	157·3	Silver	Ag	107·87
Gallium	Ga	69·7	Sodium	Na	23·00
Germanium	Ge	72·6	Strontium	Sr	87·6
Glucinum	Gl	9·02	Sulphur	S	32·07
Gold	Au	197·2	Tantalum	Ta	181·2
Hafnium	Hf	178·6	Tellurium	Te	127·7
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·0076	Thorium	Th	232·2
Indium	In	114·8	Thulium	Tm	169·4
Iodine	I	126·9	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	47·9
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·9	Uranium	U	238·2
Lanthanum	La	138·9	Vanadium	V	51·0
Lead	Pb	207·2	Xenon	Xe	130·2
Lithium	Li	7·00	Ytterbium	Yb	173·8
Lutecium	Lu	175	Yttrium	Yt	88·9
Magnesium	Mg	24·32	Zinc	Zn	65·38
Manganese	Mn	54·93	Zirconium	Zr	91·2

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INDEX OF SEPARATIONS

GENERAL methods of separation are discussed briefly in the systematic section (p. 203) under the headings of the various elements. The following index gives references to the separations that are more fully described.

Aluminium from

calcium, 305
calcium and magnesium, 282, 287
iron, 205, 283
iron and titanium, 287
lead, manganese, silica, etc., 292
manganese, nickel, zinc, etc., 203
silica, 287

Bismuth from lead, tin and cadmium, 278

Cadmium from

bismuth, lead and tin, 278
zinc, copper, etc., 300

Calcium from

iron, aluminium and magnesium, 281
iron, aluminium and phosphate, 304
silica, 287

Chromium from iron, 102, 229

Cobalt from nickel, 224, 240

Copper from

iron, 269, 274, 299
lead, cadmium, zinc, etc., 300
lead, tin, etc., 277
nickel, 181, 183, 269
silver, 267
zinc, 274

Iron from

aluminium, 205, 283
aluminium and titanium, 287
calcium, 305
calcium and magnesium, 282, 287
chromium, 102, 229
copper, 269, 274, 299
copper, lead, tin and zinc, 277
lead, manganese, silica, etc., 292
manganese, zinc, etc., 203, 229
silica, 287

Lead from

bismuth, cadmium and tin, 278
copper, cadmium and zinc, 300
copper, tin, etc., 277
silica, etc., 292
tin and antimony, 272

Magnesium from

calcium, iron and aluminium, 281
silica, 287

Manganese from

barium and iron, 302
cadmium, copper, zinc, etc., 300
iron, 203, 229
iron and aluminium, 203, 292

Nickel from cobalt, copper, iron, manganese, zinc, etc., 240
copper, 186, 269

Potassium from

all other metals, 245
calcium, silica, etc., 289
sodium, 250

Silica from metallic oxides, 253, 281, 287, 292

Silver from copper and nickel, 267

Sodium from

calcium, silica, etc., 289
potassium, 250

Tin from

bismuth, lead and cadmium, 278
copper, lead, zinc, etc., 276, 277
lead, 272

Titanium from

iron, aluminium, etc., 287

Zinc from

cadmium, copper, iron and manganese, 300
copper, lead, tin and iron, 274, 277

INDEX

- ABSORPTION apparatus for gases, 329
 pipettes, 313
 Acetic acid, volumetric determination
 of, 66
 Acidimetry and alkalimetry, 51
 Acidity of water, 355, 359, 364
 Adsorption indicators, 124
 Air-bath, 25
 Albite, 285, 420
 Albumenoid ammonia in water, 341, 363
 Alcohol, density of, 424
 Alloys, analysis of, 267
 fusible, 278
 preparation for analysis, 17
 Aluminium, 203
 as basic acetate, 203
 as oxide, 163
 bronze, 277
 in water, 361
 Ammonia, colorimetrically, 196
 direct determination of, 72
 indirect determination of, 70
 in water, 341, 363
 (table of densities), 424
 Ammonium, 206
 thiocyanate, standard, 127
 Amount of substance for analysis, 21
 Anorthite, 285
 Antimony as sulphide, 206
 volumetric determination of, 89, 117,
 139
 Arsenic, gravimetric determination of,
 207
 volumetric determination of, 116, 139
 Asbestos filter, 145
 Aspirator, 217, 220
 Atmospheric carbon dioxide, 331
 Atomic weights, table of, 428
 Azolitmin, 54, 418
- BALANCE, sensitiveness of, 7
 use of, 4, 8, 9
 Barium as chromate, 208
 as sulphate, 208
 hydroxide, standard, 64
 Baryta, standard, 64
 Basic acetate method, 203
 Beakers, 14
 Beckmann's boiling-point method, 406
 thermometer, 402, 403
 Bismuth, gravimetric determination of,
 209
 Bleaching powder, valuation of, 115,
 133, 327
 total chlorine in, 131
 Boiling-point method, 406, 409, 410
 Boiling-rod, 16
 Borate, 212
 Borax, volumetric analysis of, 66, 67
 Brass, analysis of, 274
 Bromide, gravimetric determination of,
 213
 volumetric determination of, 125,
 129
 Bromine in an organic substance, 382
 Bronze, analysis of, 276
 Büchner funnel, 17
 Bunsen burner, use of, 149
 valve, 29, 93
 Burette, 35
 calibration of, 45
 clamp, Ostwald, 65
 cleaning a, 37, 44
 fitted for constant use, 64
 reading device, 43
 Schellbach, 44
 use of, 42
 Burner, Bunsen, 149
 Méker, 150

- CADMIUM, 213
 electrolytic determination of, 186
 Calcium, 214
 as oxalate, 176, 283, 305
 carbonate in lime, 69
 purification of, 289
 chloride tube, 216
 hydroxide, determination of solubility of, 69
 hydroxide, standard, 65
 in water, 353, 361
 oxide in lime, 69
 volumetric determination of, 85, 353
 Calibration of a burette, 45
 of weights, 11
 Carbide method for determination of water, 260
 Carbon dioxide in air, 331
 in gaseous mixture, 315, 320
 preparation of pure, 148
 Carbon in an organic substance, 365
 Carbon monoxide in gaseous mixture, 317, 320
 "Carbon" tube, 201
 Carbonate, direct method, 215
 indirect method, 219
 in water, 362
 Carbonate-free sodium hydroxide, 63
 Casseroles, 15
 Cassiterite, 258, 421
 c.c. as unit of volume, 35
 Chlorate, 221
 in bleaching powder, 131
 volumetric determination of, 113, 130
 Chloride, 221
 as silver chloride, 164
 in water, 346, 363
 volumetric determination of, 125, 129
 Chlorine in an organic substance, 382
 Chlorine in bleaching powder, available, 115, 133, 327
 total, 131
 Chromate, gravimetric determination of, 222
 volumetric determination of, 103, 106, 113
 Chromium, 221
 in chrome iron ore, 102
 Clay, 285, 420
 Cleaning glass vessels, 37, 57
 Coal gas, hydrogen sulphide in, 334
 sulphur in, 329
 Cobalt, 223
 Coin, analysis of bronze, 109, 276
 analysis of nickel, 109, 186, 269
 analysis of silver, 130, 267
 Colorimeters, 190
 Colorimetric methods, 189
 Combustion apparatus, 366
 of a liquid, 374
 of a solid, 371
 pipette, 321
 Conductivity of water, 339
 Copper, 224
 as oxide, 166
 as sulphide, 174
 as thiocyanate, 225
 colorimetric determination of, 195
 electrolytic determination of, 181, 183
 gravimetric determination of, 166, 174, 225
 pyrites, analysis of, 297, 421
 volumetric determination of, 109, 278
 Copper-zinc couple, 348
 Crucible, Gooch, 145
 nickel, 146
 palau, 144
 platinum, 143
 porcelain, 142
 Rose, 147
 silica, 143
 Crucible tongs, 145
 Cubic centimetre, as unit of volume, 35
 Cupferron method for iron, 229
 preparation of, 417
 Cyanide, volumetric determination of, 126

 DECANTATION, washing by, 28
 Density of gases, 425
 determination of vapour, 391, 394
 tables, 422
 Desiccator, 16
 Diacetyldioxime (dimethylglyoxime)
 method for nickel, 240
 Dichromate, 222
 standard, 89
 Dionic water tester, 339
 Dolomite, analysis of, 281, 420
 Drying a precipitate, 150
 Dumas's method for nitrogen, 377

- EGGERTZ tubes, 201
Electrolytic methods, 178
Eosin, as indicator, 125
Error, limits of allowable, 21
Etching a line on glass, 39
Ethylene in gaseous mixture, 315, 320
Evaporation, 23
- FEATHER, trimmed, 28
Feldspar, 285
Ferric salts, volumetric determination of, 94, 134
Ferrous salts, volumetric determination of, 94
Filter, incineration of, 151
 paper-pulp, 30
 papers, choice of, 27
Filter-pump, use of, 29
 regulator for, 147
Filtration, 26
 with Gooch crucible, 145
 with paper-pulp, 30
 with suction, 29
Flasks, 15
 graduated, 35
 standardisation of, 37
Flint glass, 292, 420
Flue gases, sulphur dioxide in, 334
Fluorescein, as indicator, 124
Fluoride, 226
Formaldehyde, volumetric determination of, 68
Freezing-point method, 397
Funnels, 15, 29, 30
Fusible alloy, analysis of, 278
- GARNET, 285, 421
Gas analysis, 308
 -burette, 311
 -holder, 367
 -pipettes, 313
Gases, density of, 425
Glass, analysis of, 292, 420
Gooch crucible, use of, 145
Gravimetric analysis, 141
Grinding minerals, 18
Gun metal, 276
G.W.A. unit of volume, 36 (and *foot-note*)
- HARDNESS of water, 339, 350, 359, 363
Hempel apparatus, 311
 burette, 311
 pipettes, 313
Hydrochloric acid, constant boiling-point, 60
 influence on permanganate titration, 92
 standard, 55
 (table of densities), 422
Hydrochloroplatinic acid, 418
Hydrofluoric acid, testing purity of, 256
Hydrogen in gaseous mixture, 320
 in an organic substance, 365
 peroxide, valuation of, 81, 325
 preparation of pure, 147
 sulphide in coal gas, 334
 volumetric determination of, 112
Hydrosulphite, volumetric determination of, 111
Hypochlorite, volumetric determination of, 115, 133, 327
- IGNITION of precipitates, 148
Incineration of filter, 151
Indicators, 34, 51, 418
Iodide, gravimetric determination of, 227
 volumetric determination of, 125, 129
Iodine in an organic substance, 382
 purification of, 105 (*footnote*)
 standard, 104, 107
Iron, 228
 as basic acetate, 203
 as oxide, 159
 colorimetric determination of, 192
 gravimetric determination of, 159, 228
 in black ink, 102
 in a mineral, 99, 101, 282, 287
 in chrome iron ore, 102
 in ferric salts, 94, 134
 in iron alum, 94, 157, 159
 in iron wire, 92, 136
 in water, 361
 pyrites, analysis of, 295, 420
 volumetric determination of, 92, 94, 99, 102, 134
- JENA glass, 292
Jones reductor, use of, 95

- KAOLINITE, 285
 Kilogram (standard), 35 (*footnote*)
 Kjeldahl's method for nitrogen, 381
- LANDSBERGER'S boiling-point method, 410
 Lawrence Smith method, 289
 Lead, 230
 action of water on, 360
 as chloride, 273
 colorimetric determination of, 198
 dioxide, valuation of, 83, 113, 114
 electrolytic determination of, 187
 gravimetric determination of, 230
 in water, 359, 364
 Lime, determination of solubility of, 69
 manganese in, 200
 volumetric analysis of, 69
 water, standard, 65
 Limestone, analysis of, 281
 Litmus solution, preparation of, 418
 use of, 52, 53, 54
 Litre, as unit of volume, 35
 Logarithms, table of, 426
 Lubricants for glass taps, 42
 Lumsden's vapour density method, 394
 Lunge nitrometer, 323
- MAGNESIA mixture, 207, 417
 Magnesium, 232
 as pyrophosphate, 172, 284
 in water, 353, 361
 Manganese, 232
 by bismuthate method, 87
 colorimetric determination of, 199
 dioxide, volumetric determination of, 82, 113
 analysis of crude, 302, 421
 gravimetric determination of, 232
 in steel, 88, 200
 volumetric determination of, 87
 Manganite, analysis of, 302, 421
 Méker burner, use of, 150
 Mercury, 235
 gravimetric determination of, 235
 volumetric determination of, 130
 Metals, preparation for analysis, 17
 Methane in gaseous mixture, 320
 Methyl orange solution, preparation of, 418
 use of, 52, 53
 Methyl red solution, preparation of, 418
 use of, 52, 53, 54
 Mica, 285
 Millilitre, 35
 Minerals, preparation for analysis, 17
 ml. as unit of volume, 35
 Mohr's "cubic centimetre," 36
 Molar weights, determination of, 390
 Monax glass, 14
 Mortar for hard minerals, 19
 Muscovite, 285
- NESSLER solution, 197
 tubes, 191
 Newton's alloy, analysis of, 278
 Nickel, 238
 colorimetric determination of, 201
 electrolytic determination of, 185
 gravimetric determination of, 238
 Nickel coin, analysis of, 186, 269
 copper in, 109
 Nitrate, 74, 84, 323
 in water, 348, 364
 volumetric determination of, 74, 84
 Nitric acid (table of densities), 423
 Nitrite, 83, 323, 325
 in water, 347, 364
 volumetric determination of, 83
 Nitrogen in gaseous mixture, 320
 in an organic substance, 376, 381
 in nitrate or nitrite, 323, 325
 Nitrometer, Lunge, 323
 Schiff, 378
 Normal solution, definition of, 32
- ORES, preparation for analysis 17
 Organic analysis, 365
 Orthoclase, 285, 420
 Ostwald burette clamp, 65
 Oxalate, volumetric determination of, 81
 Oxidation and reduction processes, 33
 Oxygen in gaseous mixture, 316, 320
 preparation of pure, 321 (*footnote*)
- PALAU crucibles, use of, 144
 Paper mats, use of, 16
 Paper-pulp filter, 30
 Parallax, error due to, 42, 43, 44
 Penfield's method for water in minerals, 261

- Perchloric acid, 248 (*footnote*)
(table of densities), 423
- Percussion mortar, 19
- Permanent hardness of water, 350, 351
- Permanganate, standard, 77
titrations in presence of hydrochloric acid, 92
- Peroxides, determination of, 81, 325
- Phenolphthalein solution, preparation of, 418
use of, 52, 53, 54
- Phosphate, gravimetric determination of, 241
in a mineral, 285, 291
in superphosphate manure, 306
in water, 349
volumetric determination of, 75
- Phosphorus in steel, 76
- Pipe-clay triangle, 144
- Pipette, 35
standardisation of, 39
use of, 39
- Platinum crucibles, use of, 143
- Potassium, 244
bromate, standard, 139
cyanide, volumetric determination of, 126
dichromate, standard, 89
ferrocyanide, standard, 136
hydroxide solutions (table of densities), 424
vapour pressure of, 425
in insoluble silicate, 289
permanganate, standard, 77
pyrosulphate, fusion with, 100, 283, 287
thiocyanate, standard, 127
- Precipitates, drying of, 150
ignition of, 148
washing of, 28, 161
- Precipitation, general instructions regarding, 25
- Pressure regulator for filter-pump, 147
- Purification of salts, 16
- Pyrex glass, 14, 292
- Pyrites, analysis of, 295, 297, 420, 421
- Pyrolusite, analysis of, 302, 421
valuation of, 82, 113
- Pyrosulphate, fusion with, 100, 283, 287
- REAGENTS, list of common, 415
used in gas-pipettes, 315
- Recrystallisation of salts, 17
- Red lead, valuation of, 83, 113, 114
- Reduction of ferric salts, 94, 134
- Robertson's method for halogens, 383
- Rocks, preparation for analysis, 17
- Rose crucible, use of, 147
- Rose's alloy, analysis of, 278
- Rotating electrode, 183
- Rubber, permeability to gases, 310
- SAMPLING a gas, 309, 312, 313
minerals and ores, 17
water, 337
- Schellbach burette, 44
- Scoop for weighing, 20
- Silica, 252
crucible, 143
in insoluble silicate, 253, 286, 292
in water, 361
plate for excluding flame gases from crucible, 144
- Silicate, analysis of insoluble, 285, 292
- Silver coin, analysis of, 130, 267
- Silver, gravimetric determination of, 257
nitrate, standard, 121, 127
volumetric determination of, 130
- Soda-lime tube, 216
- Sodium, 244
arsenite, standard, 108, 133
hydroxide, carbonate-free, 63
preparation of pure, 167
standard, 61
(table of densities), 424
in insoluble silicate, 289
thiosulphate, standard, 104, 110
- Soft water, 335, 339, 350, 359, 363
- Solder, analysis of, 271
- Standard flask, 37
litre, 35
pipette, 39
solutions for analysis, 418
solutions (general notes), 32, 47
solutions of desired concentration, 49
- Standardisation (use of term), 36
of a flask, 37
of a pipette, 39
- Starch solution, 105
- Steam-bath, 23, 24

- Steel, manganese in, 88, 200
 phosphorus in, 76
 Stirring-rod, 15, 28
 Sulphate, gravimetric determination of, 169
 in copper sulphate, 70
 Sulphide, 258
 volumetric determination of, 112
 Sulphite, volumetric determination of, 111
 Sulphur in coal gas, 329
 in an organic substance, 387
 in minerals, 296, 298, 302
 Sulphur dioxide in flue gases, 334
 Sulphuric acid, standard, 60
 (table of densities), 422
 volumetric determination of, 68
 Sulphurous acid, volumetric determination of, 111
 Superphosphate, analysis of, 304
- TALC, 420
 Tare of a crucible, 151
 Temporary hardness of water, 350
 Thiocyanate, standard, 127
 Thiosulphate, standard, 104, 110
 Tin, 258
 volumetric determination of, 118, 120
 Titanium, 259
 colorimetric determination of, 194
 in iron ore, 195
 in silicate rock, 287
 Titanous chloride, standard, 134
 Type metal, 89, 140, 271
- UNIT of volume, 35
- VALVE for wash-bottle, 29
 Vapour density, determination of, 391, 394
 Vapour pressure of potassium hydroxide solutions, 425
 of water, 425
 Victor Meyer's vapour density method, 391
 Vinegar, acetic acid in, 66
 Volume of 1 gram of water, 37
 Volumetric analysis, 31
- WALKER - LUMSDEN'S boiling-point method, 410
- Wash-bottle, 14, 29
 Washing of precipitates, 28, 161
 Water, acidity or alkalinity of, 355, 364
 action on lead, 360, 364
 "alkalinity" of, 351, 352, 362
 aluminium in, 361
 ammonia-free, 197
 ammonia in, 341, 363
 analysis, 335
 calcium in, 353, 361
 carbonate in, 362
 chloride in, 346, 363
 colour of, 339
 conductivity of, 339
 gravimetric determination of, 156, 157; 260
 hardness of, 339, 350, 359, 363
 iron in, 361
 lead in, 359, 364
 magnesium in, 353, 361
 nitrate in, 348, 364
 nitrite in, 347, 364
 odour of, 338
 organic matter in, 341, 344, 364
 phosphate in, 349
 potassium in, 362
 salts in, 335, 361
 silica in, 361
 sodium in, 362
 softness of, 335, 339, 350, 359, 363
 solids in, 340, 363
 sulphate in, 362
 taste of, 339
 total solids in, 340, 363
 turbidity of, 338
 vapour pressure of, 425
 Weighing-bottle, 20
 -pipette, 401
 -scoop, 20
 Weighing "by difference," 19
 Weighing, method of, 5, 8
 Weight of 1 c.c. of water, 37
 of substance for analysis, 21
 Weights, calibration of, 11
 Wood's alloy, analysis of, 278
- ZINC, 262
 blende, analysis of, 300, 421
 dust, valuation of, 327
 gravimetric determination of, 168, 262
 volumetric determination of, 136



12 OCT 1932 N.Y.S. 10/14/32

